TO STUDY THE ROLE OF SURFACTANTS ON THE ION EXCHANGE BEHAVIOUR OF SOME FIBROUS AND NON-FIBROUS MATERIALS

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF

Master of Philosophy

IN

APPLIED CHEMISTRY

BY

MISS AMITA SOMYA

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF ENGINEERING & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH U.P. (INDIA)

2005

Off. (0571) [illegible]
Res. (0571) [illegible]
Email: chairmanapcd@[illegible]

DEPARTMENT OF APPLIED CHEMISTRY

Chairman

FACULTY OF ENGINEERING & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH - 202002 (INDIA)

Certificate

This is to certify that the work presented in this dissertation entitled **"To study the role of surfactants on the ion exchange behaviour of some fibrous and non-fibrous materials"** has been carried out by **Ms. Amita Somya.** It is an original contribution of the candidate and is suitable for submission for the award of M.Phil degree in Applied Chemistry.

Dated: 7/5/05

H S Rathore

Prof. H.S. Rathore
(Supervisor & Chairman)

Applied Chemistry Department
Aligarh Muslim University
Aligarh-202002
Tel. : (0571) 2700920 Ext.:3001

Prof. (Dr.) K. G. Varshney
Ph.D.,D.Sc.
Emeritus Fellow (AICTE)

Dated.....

Certificate

This is to certify that the work presented in this dissertation entitled **"To study the role of surfactants on the ion exchange behaviour of some fibrous and non-fibrous materials"** has been carried out by **Ms. Amita Somya.** It is an original contribution of the candidate and is suitable for submission for the award of M.Phil degree in Applied Chemistry.

Dated: 7/5/05

Prof. K.G. Varshney
Emeritus Fellow (AICTE)

Resi. :SHANTI SADAN, 18/158, Pakki Sarai, Aligarh-202001
Tel. : 0571-2411931 Mobile : 9412172929
e-mail : roma_gopal@rediffmail.com

ACKNOWLEDGEMENT

I prostrate in reverence to God, the omnipotent and omniscient, Who gave me the required inspiration in completing this academic dissertation.

It gives me immense pleasure and honour in expressing my profound sense of gratitude and obeisance to Dr. K.G. Varshney, Ph.D., D.Sc., Professor Emeritus, Department of Applied Chemistry, A.M.U., Aligarh, for his painstaking perseverance in steering me out of the labyrinthine straits. His sympathetic and kind encouragement, with timely help, has been the source of inspiration throughout this work. No words can adequately express my heartful gratitude and fathomless indebtedness to him, my reverend teacher, guide & supervisor.

I express my heavy debt of gratitude towards Prof. H.S. Rathore, Chairman, Department of Applied Chemistry, A.M.U., Aligarh, for providing the necessary facilities to complete the work successfully.

My sincere thanks are due to Dr. M.Z. A. Rafiquee, Senior Lecturer, Department of Applied Chemistry, A.M.U., Aligarh, for the fruitful suggestions and guidance in the field of surfactants.

My sincere thanks are also due to Dr. M. Drabik, Senior Scientist, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia, for helping in the TGA/DTA studies of the materials under investigation. Further, I acknowledge with thanks the technical assistance provided by the Institute of Instrumentation Centre, IIT., Roorkee, All India Institute of Medical Sciences, New Delhi, and the Regional Sophisticated Instrumentation Cente, Central Drug Research Institute, Lucknow.

I express my gratitude to all my friends and colleagues in the Department, especially, Mr. Arun Agrawal and Mr. Abdul Asif Jilani, for their kind co-operation, day-to-day help and academic discussions.

Finally, it is my most sincere acknowledgement and reverence to my loving parents for their affection and blessings, which has been a perennial source of inspiration for me in the successful completion of this task.

Amita Somya

Ms. Amita Somya

Dedicated

to

My Loving Parents

CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter - 1
Introdution

INTRODUCTION

Historically, chemistry could be divided into five main areas: Analytical, Biochemical, Inorganic, Organic and Physical. It is rather impossible to make such a division in recent years, because analytical chemistry, like other areas of chemistry and science, has gone through drastic changes and growth. At present chemists or scientists are busy in crossing from one area to another and frequently, chemists who call themselves as organic chemists, are busy in physical chemistry; likewise analytical chemists are doing organic or inorganic chemistry and so on. Not even this, but new areas, such as chemical physics, biophysics and molecular biology are rapidly developing because of the crossover of scientists from one area to another. Many advances and changes in these areas were made possible by analytical results. Hence, it will not be amiss to say that analytical chemistry is necessary for growth and development of science and technology and it must be integrated with other scientific and chemical disciplines.

The discipline of analytical chemistry consists of qualitative and quantitative analyses. The former deals with the identification of elements, ions or compounds present in a sample, while the latter deals with the determination of how much of one or more constituents is present. The sample may be solid, liquid, gas, or a mixture.

Analytical chemistry seeks ever improved means of measuring the chemical composition of natural and artificial materials. The techniques of this

science are used to identify the substances which may be present in a material and to determine the exact amounts of the identified substance.

Separations are extremely important in analytical chemistry. The goal of an analytical separation is, usually, to eliminate or reduce interferences so that quantitative analytical informations can be obtained about complex mixtures. There is a variety of separation methods that are in common use, including precipitation, distillation, solvent extraction, crystallization, dialysis, ion-exchange, chromatography, electrophoresis, field flow fractionation etc.

Of all the different types of separation methods, chromatography has the unique position of being applicable to all types of problems in all branches of science. It has undergone explosive growth in the last 30 years. The chromatographic technique was first invented by a Russian botanist *Mikhail Tswett* in 1906, at the university of Warsaw. He coined the term "*Chromatography*" from the Greek words "*chromatos*" and "*graphy*" which mean "color" and "to write" respectively. The International Union of Pure and Applied Chemists (IUPAC) has drafted a recommended definition of chromatography: "*Chromatography is a physical method of separation in which the components to be separated are distributed between 2 phases, one of which is a stationary phase, while the other is a mobile phase*" [1]. Since its discovery, this technique has undergone tremendous modifications and now a days various types of chromatographic techniques have been developed for separating almost any kind of a given mixture, whether coloured or colourless

into its constituents and to test the purity of these constituents. The applications of chromatography have grown explosively in the last fifty years, owing not only to the development of several new types of chromatographic techniques, but also due to the growing needs of scientists for better methods of separating the complex mixtures or metal ions [2]. Various chromatographic methods are summarized in Table 1.1

Out of these several chromatographic methods, *ion exchange* has gained great attention by analysts in practice. The phenomenon of ion exchange is not of a recent origin. The earliest of the references were found in the Holy Bible establishing Moses' priority who succeeded in preparing drinking water from brackish water, by an ion exchange method [3]. Later on, Aristotle found that sea water loses part of its salt contents when percolated through certain sand [4]. A scientific study of this process was made in the mid of the 19th century [5, 6] and the ion exchange properties were explored [7]. Harms and Rumpler [8], synthesized the first aluminosilicate based ion exchangers in 1903. Folin and Bell [9] first developed an analytical method for the collection & separation of NH_3 from urine in 1917 by synthetic zeolites. Perhaps Dr. Gans [10] in Germany was the first person who used ion exchanger to an industrial scale. Thereafter, a lot of scientific work has been done on natural, processed and synthetic inorganic materials for their ion exchange properties. In 1935, Adams and Holmes [11] synthesized some synthetic high molecular weight polymers containing a large number of functional groups.

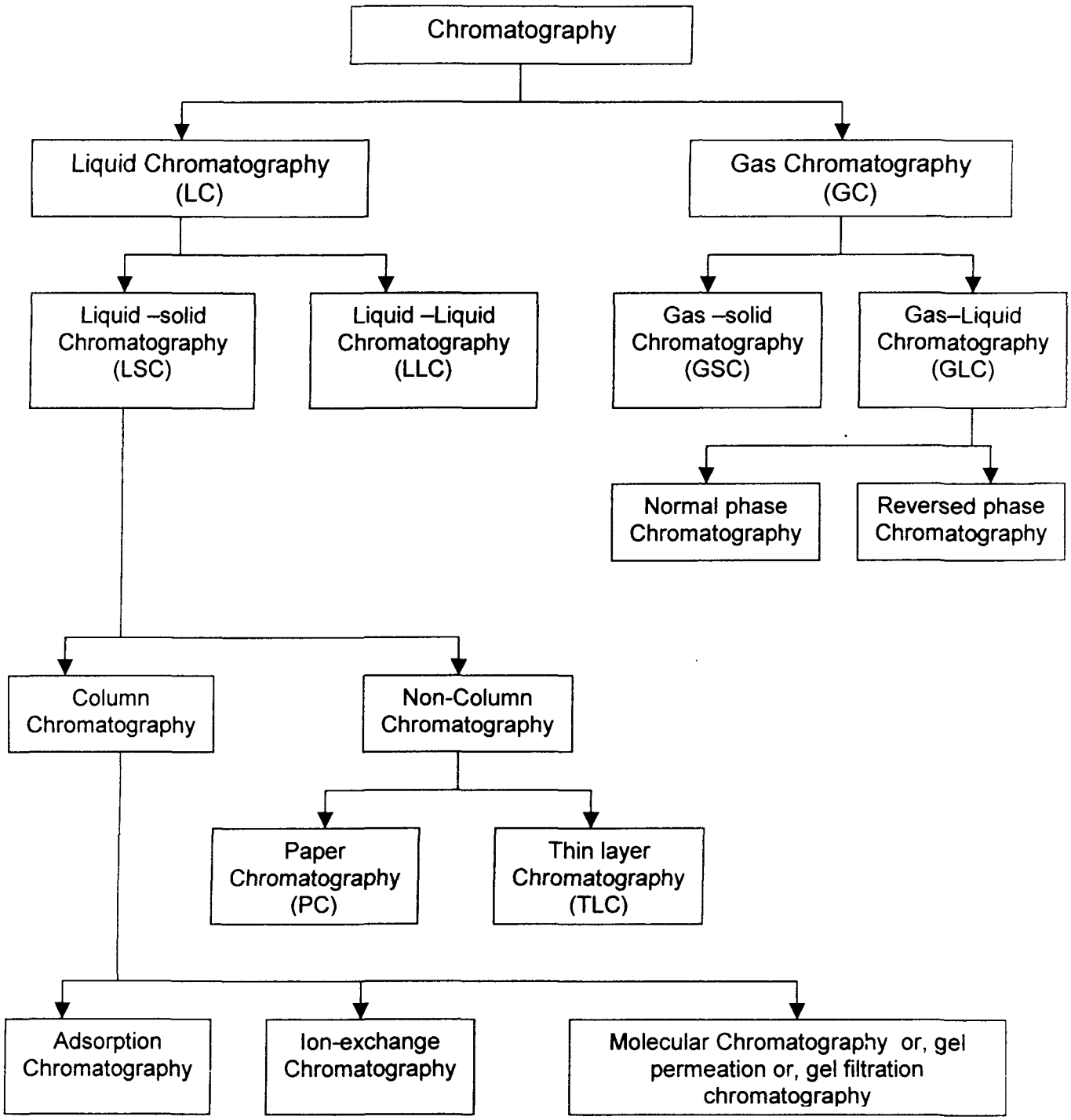


Table. 1.1 Various Chromatographic techniques used in Analytical Chemistry

They are known as organic ion exchangers. The period after 1935 has seen a rapid development of synthetic organic and fibrous ion exchangers.

Although at first the ion exchangers were used for water softening but later on they were employed in various fields like separation of metal ions, separation of organic substances, preparation of ion selective electrodes, preparation of fuel cells and preparation of artificial kidney machines. Thus, the ion exchange process has been established as an analytical tool in laboratories and industries.

Ion exchangers are insoluble solid materials containing exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign on contacting with an electrolyte solution. Depending upon their ability of exchanging cations or anions, the ion exchangers are either '*cation*' or '*anion*' *exchangers* respectively. Certain materials are capable of both cation and anion exchange. They are called as '*amphoteric' ion exchangers*. A cation exchanger comprises a matrix with negative charge while an anion exchanger comprises a matrix with a positive charge. The negative or positive charge of the matrix is compensated by the oppositely charged counter ions, which are mobile in nature. A typical ion exchange reaction may be represented as follows:

$$R\text{–}A + B\ (aq) \longrightarrow R\text{–}B + A\ (aq)$$

where A & B are the replaceable counter ions, R is the structural unit (matrix) of the ion exchanger and aq stands for the aqueous phase. This process is

reversible, i.e., it can be reversed by suitably changing the concentration of the ions in solution.

On the basis of the nature of the matrix, an ion exchanger may be '*organic*' or '*inorganic*' in nature. Organic ion exchangers, commonly known as "*ion exchange resins*" are well known for their uniformity, chemical stability and for the easy control over their ion exchange property through synthetic methods. Organic ion exchange resins consist of a cross-linked hydrocarbon matrix containing ionogenic groups. The charge of the groups is balanced by mobile counter ions. These resins may be natural or synthetic. The matrix of ion-exchange resins can be formed by condensation or addition polymerization. Then, the fixed ionic groups are introduced. The matrix carries ionic groups such as $-HSO^-_3$, $-COO^-$, $-HPO_3^-$ etc in cation exchange resins and $-NH_3^+$, $>NH_2^+$, $>N^+<$ etc. in anion exchange resins. Anion and cation exchange resins may be weak or strong depending upon the presence of ionic groups. Synthetic resins are superior to the natural resins in their high chemical and mechanical stability, ion exchange capacity and ion exchange rates etc.

Organic resins have wide applications in analytical chemistry because of their high stability in the wide range of pH and reproducibility in the results. but their instability under the conditions of high temperature and strong radiations led to the development of *inorganic ion exchange materials*. Since inorganic ion exchangers are capable of being stable at elevated temperatures and in the presence of strong radiations, they have wide applications in nuclear

researches such as radioisotope separations and nuclear waste treatments etc. They have also been found applicable in the determination and detection of metal ions in pharmaceutical and biological products, analysis of alloys and rocks, as ion-selective electrodes, as packing materials in ion chromatography, and as catalysts. They also find application in environmental analysis [12]. Inorganic ion exchangers are generally the oxides, hydroxides and insoluble acid salts of polyvalent metals, heteropoly acid salts and insoluble metal ferrocyanides. They can be prepared both in crystalline and amorphous forms and have good chemical stability, reproducibility in ion exchange behaviour and selectivity for certain metal ions. Important advances in this field have been reviewed by a number of workers/researchers at various stages of its development, such as Amphlett [13], Fuller [14], Qureshi et al. [15], Vesely and Pekarek [16], Clearfield et al. [17,18], Alberti et al. [19,20], Castantino [20] and Varsheny et al. [21]. The books [22],23] published in this field have provided a complete picture and thorough insight of this field and its widespread applications. Dyer [24,25] has dealt with the theories involved zeolite molecular sieves, which have principles underlying the inorganic ion exchangers.

Alberti (Italy) and Clearfield (USA) devoted most of their studies on the crystalline inorganic ion exchangers. However, the research group of Qureshi (India) started their studies mainly on the amorphous materials [26-33] Varshney et al. extended this work and synthesized a large number of inorganic

ion exchangers and explored their applications in the environmental analysis [34-44].

However, the main drawback of these materials has been that they are not very much reproducible in behaviour. Further, they are found not to be chemically and mechanically very stable perhaps due to their inorganic nature. So, an interest was developed to obtain some organic based inorganic ion exchangers. They are expected to have chemical inertness, good mechanical stability, and high temperature and radiation resistance. These exchangers may also be termed as *hybrid ion exchangers* as they consist of both the organic and inorganic parts. This new class of ion exchangers have been prepared in these laboratories by incorporating a polymeric organic material into the inorganic ion exchange matrix [45-49].

Very recently, *fibrous ion exchange materials* have drawn attention of researchers and technologists as they exhibit a high efficiency in the process of sorption from gaseous and liquid media. Fibrous ion exchangers can be used in the form of various textile goods, such as cloth, conveyer belts, non-woven materials, staples, nets etc., opening up new possibilities for many technological processes. These materials consist of monofilaments of uniform size ranging in diameter between 20-300 μm. This predetermines short diffusion path of sorbent and high rate of sorption that can be about 100 times higher than that of the granular resins with a particle diameter of 0.25-1 mm, normally used in such processes. Hence, they are more applicable in large scale

processes and are of great importance nowadays [50-53]. An important advantage of fibrous ion exchangers has been their extremely high osmotic stability that allows them to be used in the multiple wetting and drying processes occurring at cyclic sorption/regeneration operations in air purification. The variants of application of fibrous ion exchange materials are illustrated in Fig.1.1.

There are a number of monographs [54,55] reviews [56,57] and patents in which preparations, properties, technologies, and possible areas of applications of fibrous ion exchangers are described. Recently, at the Institute of Physico-organic Chemistry of the Byelorussion Academy of Sciences (Russia), intensive research has been carried out for developing preparation methods for different types of fibrous ion exchangers, and to identify the fields of their applications such as, air purification from acidic and alkaline impurities [58], preparative chromatography, water purification or extraction of ions of useful elements from gaseous media. The processes of water purification and extraction of useful substances as uranium, gold etc. from water, were carried out by Japanese and Western workers [59-61].

Fibrous ion exchangers, developed by Soldatov, have the registered trademark "Fiban® [62]. They are [63] strong acid cation exchangers, prepared by sulphonation of styrene divinyl benzene copolymer grafted onto polyprophylene (PP) fibre. Fiban A-1 [64] is a strong base fibre and prepared by chloromethylation and subsequent amination of the same grafted copolymer

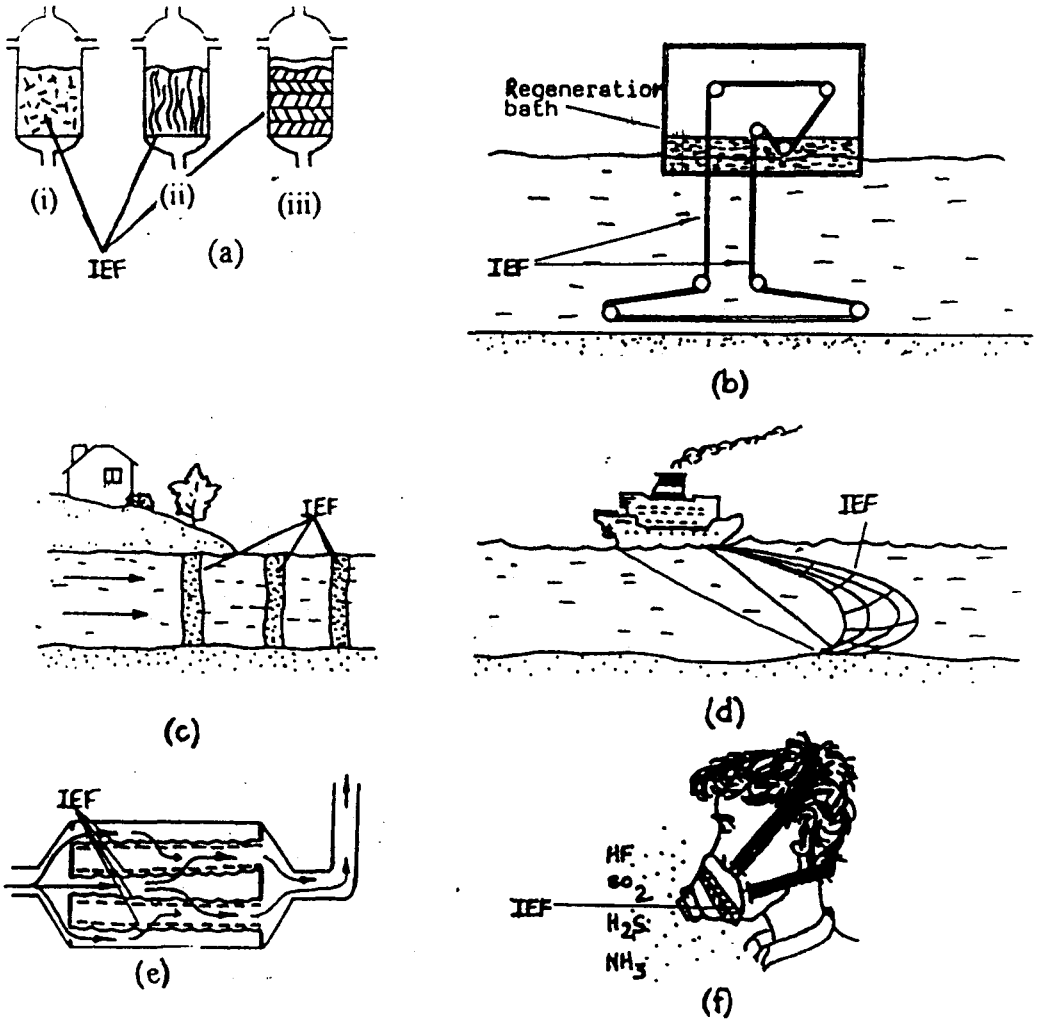


Fig.1.1 Variants of application of ion-exchange fibres (IEF) in liquid and gaseous processes.

(a) Ion-exchange columns with different filling
(i) Staple pulp (ii) Parallel threads (iii) Layers of fibrous material

(b) Coveyer belt made of ion-exchange fibres (Process with continuous regeneration).

(c) Mats made of IEF in the river or sea stream.

(d) Dragging nets made of IEF.

(e) Chemical air filters with IEF.

(f) Gas mask or respirator filled with IEF material.

with trimethylamine. Fiban K-1 (cation) and A-1 (anion) ion exchangers are analogous to the common granular ion-exchange resins and can be used for the same purpose. The fiban AK-22 is a weak base polyacrylic fibre. It is a complex forming polyampholyte containing imidazoline and carboxyl groups [65-66]. The most extensive studies in this field have been made in a number of institutes in Russia [67-69] and Japan (Toray Industries) [70-71].

Two families of fiban fibres have been developed. One of them is prepared by grafting polystyrene (PS) onto PP fibres at room temperature. It was carried out by the production of radicals in PP matrix initiated by 100 rad/s radiation. In other cases, about 2% vinyl benzene (VB) was added to the styrene. Fig.1.2 shows the scheme for preparation of the family of fibrous fiban ion exchangers.

The exchange capacity of these materials can be varied by changing the amount of polystyrene (PS) grafted onto PP fibres and degree of polymer analogous transformation. The grafting degree can be raised upto 600% (6 wgt parts of PS per one weight part of PP), the sulphonation degree to 1. amination degree to 1.2. The ion exchange capacity of these ion exchangers can be raised upto 4.5 meq/g. The problem in the synthesis of IEF is compromisingly high exchange capacity and their mechanical properties (tensile strength and elasticity). An increase in ion exchange capacity leads to a decrease in the mechanical and textile characteristics. It is also important that swelling of fibres should be maintained within acceptable limits.

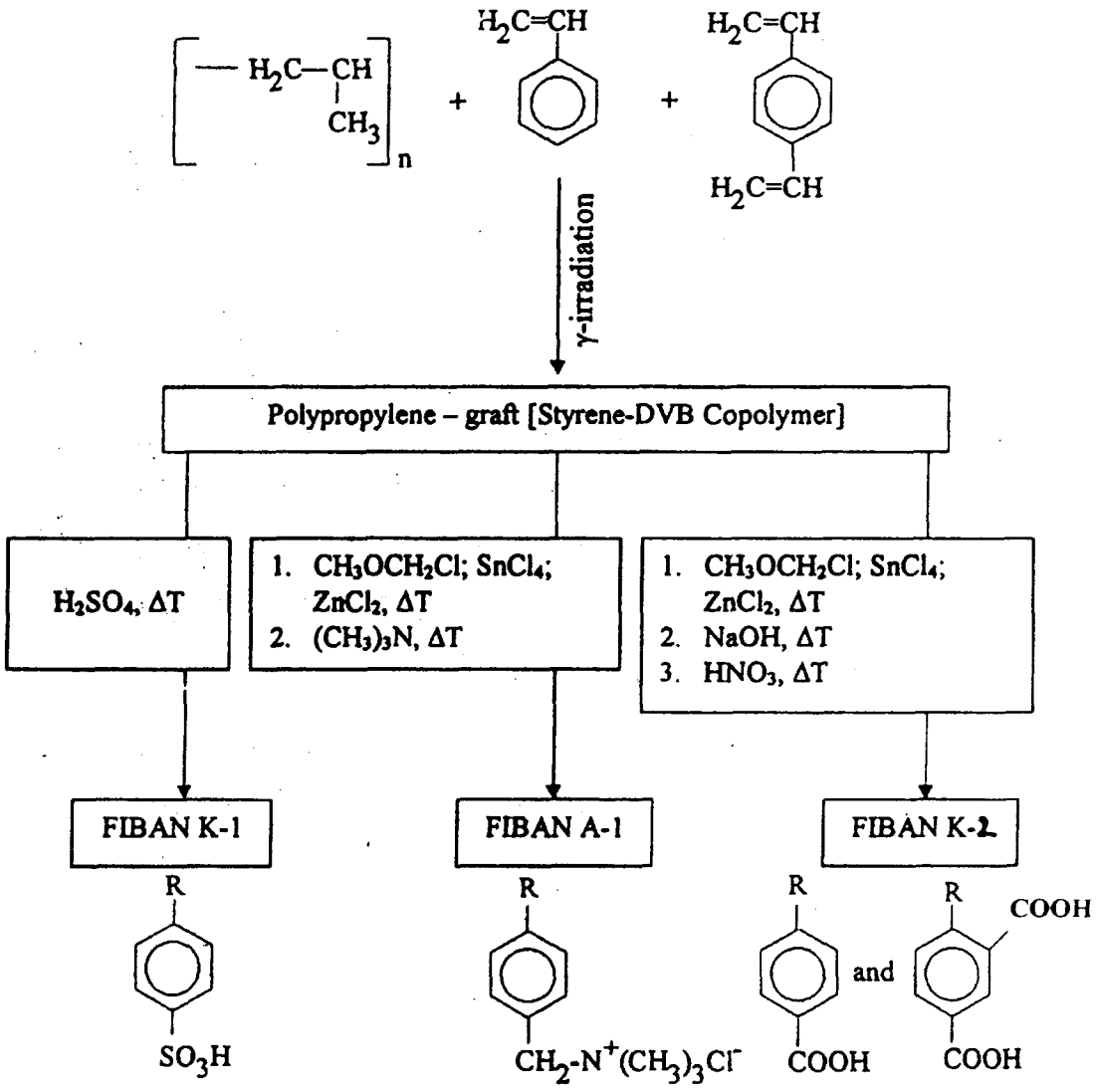


Fig.1.2 A technological scheme for preparation of Fiban ion exchangers.

The swelling of fibrous ion exchangers can be varied by changing the grafting degree of PS, the DVB content, the number of functional groups, the grafting condensations and treatment of fibres.

Various acrylic fibrous ion exchangers were prepared from time to time having good ion exchange and adsorption behaviour. They have shown applications in the separation of metal ions and as filters.

The acrylonitrile (AN) copolymer fibre cross-linked with hydrazine sulfate is a weakly acidic cation exchanger [73]. It is prepared by the hydrolysis of AN copolymer fibre under basic conditions followed by cross-linking with hydrazine sulfate. It has high ion exchange capacity, i.e., 8.4 m mole/g and good physicomechanical properties.

The amidoximated propylene containing acrylonitrile (AOPP-g-AN) fibrous ion exchanger was prepared by Hwang et al. [74] at the Chunganam National University Daejon, S. Korea. They studied the adsorption characteristics in brine water, by changing the column height. The swelling ratio of AOPP-g-AN in fibrous ion exchanger was found to be 8.54 g/g for H_2O and 8.87 g/g for H_2O_2 solvent. The ion exchange capacity depends upon the degree of grafting and shows the maximum, (3.99 meq/g) at 100% degree of grafting. Another ion exchange complex fibres were manufactured by Hwang et al. [75] by polymerizing AN and tetraethylene glycol dimethacrylate in 1:0.05: 0.5 (mol/mol) under a nitrogen atmosphere by using an inorganic solvent distribution followed by an amideoxime process for producing an

adsorbent by reacting with the product with hydroxylamine solution 2:3 times (w/v) under N_2 atmosphere; the dried adsorbent 1:0.05:0.5 (wt/wt) is then mixed and agitated to produce a mat. These ion exchange complex fibres are used for isocyanation of U, Li, B etc in sea-water and mine wastewaters.

AN-based ion exchanging fibres were produced by Orlova et al. [76] by treating AN fibres for 85-95 min at 150-160°C with a solution of polyethylene polyamine (PEPA) and a solution of NaOH (0.2-0.3%) in glycol and simultaneously performing fixation of fibre tow, having the ratio of basic and acidic groups in the final fibre, 5:1. These fibres have high sorption capacity for Hg^{+} & Cr^{+6} ions, i.e., 1,200 meq/g and 312 meq/g respectively. Hence, they can be used for the removal of heavy metal ions from industrial waste waters.

The carbonyl group containing PAN fibres were prepared in St. Petersburg, Russia [77] in which ion exchanger capacity depends on the contents of both the carbonyl group as well as the heteroconjungated structures. In these, heteroconjugated structures can function as anion or/and cation exchangers. The PANF based other ion exchangers were manufactured by Barash [78], by treating PANF with aq. hydrazine hydrate and NaOH solution containing NH_3. The IEF of multifunctional groups was synthesized [79] by using PANF as a raw material. The structure of this material was analysed by elemental analysis and IR spectrometry. The adsorption capacities and distribution coefficients for various metal ions such as Au (III), Pd(II), Pt (IV), Ru(IV), Rb(III), Os (IV), Ir(IV) were determined. The IEF were found to have

excellent adsorption and desorption properties. It is used for the separation and preconcentration of Au(III), Pd(II), Pt(IV) in the synthetic aqueous samples with the relative standard deviation 1.79-2.00% and the recovery 95.0-97.5%.

The PAN-PEPA ion exchange fibres are weakly basic anion exchangers in OH^- & Cl^- forms [80]. The sorbents based on PEPA-modified PAN Fibres are used for concentration of Mo, W, Va, Cr, As and for the extraction of these elements from natural and wastewaters. Fibrous ion exchangers having increased ion exchange capacity, were manufactured [81], by the treatment of PAN fibrewaste with (1:17) H_2SO_4-hydroxylamine sulfate mixture and simultaneous neutralization with Na_2CO_3 or alkali during heating at 40-50°C.

The polypropylene (PP) fibres grafted with acrylic acid (AAc) was used as weakly acidic ion exchanger [82]. The fibrous PP waste optionally oxidized underwent modificaton via AIBN, or benzoyl peroxide – initiated grafting of AAc in Xylene-DMF medium. The grafting reaction and properties of PP fibre and ion exchanger based on AAc-grafted PP fibres were studied by Novoselova et al. [83].

In Japan Vilene Co., Ltd., Japan, ion exchangeable fibre sheet and its production method was developed [84]. For that, the core sheath fibre of AAc-ethylene copolymer was prepared having ion exchange capacity of >2 meq g. Thus a blend fibre web of PP core/ethylene-methacrylic acid copolymer sheath was grafted with a solution comprising AAc 30, benzophenone 0.1, iron sulfate o.4, nonionic surfactant 1.0, polyethylene glycol 10 and water 58.5 wt% with

Hg light and the web had graft rate 27% and ion exchange capacity 2.7 meq/g. The manufacturing, properties and applications of high-functional fibre-sheets such as fluoro-polymer sheets, poly (p-phenylene benzobisoxazole) sheets, ion exchange resin sheets had been developed by Mogi, Katsumi in Japan [85].

The sulfonated polypropylene containing AAc/Styrene [PP-g-(AAc/Sty)], multifunctional cation exchangers were prepared [86] by the irradiation grafting of AAc and styrene onto PP stable fabric with e^- beam acceleration and its subsequent sulphonation.

Novoselova et al. had prepared the styrene-grafted PP fibre [87] by graft polymerization of styrene to PP fibre waste in the presence of AIBN and benzoyl peroxide. The fibrous ion exchanger was obtained by sulphonation of the graft copolymers. Various anionic groups, were, then fixed on this material. This fibrous ion exchanger was the most effective ion exchanger for the selective recovery of gold in the presence of other metal cyanides [88]. The gold loading capacities and selectivities of functionalised fibres with strong base or guanidine functional groups were compared favourably with conventional anion exchange resin.

The columns packed with ion exchange fibres (IEFs) (manufactured from polystyrene & reinforcing polyethylene) were prepared in Toray Industries, Japan [89]. These columns have diameter (D, 5-50 cm) and lengths (L, 2-70 cm) at L/D = 0.04-6, & packing density 0.10-0.30 gm/cc. These are used for water purification.

The polystyrene (PS) fibre graft copolymerisation with acrolein and ion exchangers based on them were prepared having amphoteric properties [90]. They were prepared by radiochemical graft polymerization of acrolein onto PP fibres followed by amination of graft copolymers with diethylene triamine. The ion exchange properties depends on the nature of graft polymers, solvent (water, acetone etc.) and irradiation dose.

The PP fibre waste was modified [91] by oxidation for introducing the grafting sites. These oxidized/modified fibres were characterized and then AAc was grafted onto these oxidised PP fibres.

Zeng et al. prepared advanced functional fibres especially activated C-fibres, ion exchange fibres and chelating fibres [92]. These fibres are used in waste gas treatment, recovery of precious metals, separation of rare earth metals, waste water treatment and in the environmental protection [93].

The VION-chemisorptive fibre in concentrated hydrazine hydrate solution were prepared [94] and the mechanism of reaction of nitrogen fibre with hydrazine hydrate in aqueous and alcoholic solution were studied. The sorption capacity of these anion exchange fibres was found to be 3 meq g. These fibres exhibit satisfactory mechanical properties.

The modern development of Hollow fibres (HF) and their applications in membrane technology for the separation of gaseous & liquid mixtures and analyses were carried out by E.M. Aizenshtein [95].

The purification of IEFs were carried out by Nakayama et al. at Toray. Industries, Japan [96] by heating at ≥ 80°C and/or treated with ≥80° water. Thus, multicore sea-island structured fibres having polystyrene and 50% polyethylene was treated with H_2SO_4 and paraformaldehyde and dried at 120° to give an ion exchanging fibre, which (6 parts) was mixed with 2 parts natural pulp to give a paper showing H_2SO_3 and HCOOH gas generation ≤ 0.07 & 2.7 μg respectively.

The modification of IEFs polycaproamide fibre was carried out by N.V. Smirnova and G.A. Gabrielyan [97]. The modification can be done by 2 ways – (i) by impregnating the initial fibre with an aq. solution of a complex salt of Cu-sulphate with Trilon-B and (ii) by grafting with methacrylic acid in the presence of $K_2S_2O_8$–$Na_2S_2O_3$.

K.E. Perepelkin, at St. Petersburg, [98] described the main types of "classic" synthetic polymeric fibres. These polymeric fibres with high thermal or chemical stability, low combustibility, high electrical conductance, adsorption capacity or ion exchange ability, are used in textile industries.

The IEFs are used in air filters. These air filters are useful for removing dusts and salts from air in clean rooms and clean booths etc. [99]. The filtering materials are made of Ag^+ exchanged ion exchangers (as antibacterial agents), fibrous ion exchanger and activated C-powder or fibrous activated carbon [100-101] by shaping with binders. The apparatus for gas filtration is composed of a filter installed in the gas circulation passage of clean room, whereas the filter is

made of ion exchange fibre cloth and supported with a pair for rails on both ends. It is used [102] for the removal of ions from gases. The filtering apparatus for water deminesalisation, have a cylindrical shape with inlets and outlets loaded with layers for ion exchanger [103]. The water demineralisation by ion exchangers is characterised by direct and counter-current filtration/permeation of water flow, sample design, low investment costs and production of water of high purity.

Endo et al., at Ebara Corp. Japan, used IEFs in air purifier for cleaning room of semiconductor industry [104], etc. The air purifier comprises a casing of rectangular frame, flat filter cassettes, which are formed from pleat-shape folded IEFs, arranged in the casing and the filter cassettes are detachably mounted in the casing to form horizontally oriented V-shaped pairs. The filter cassettes have thickness 50-70 mm and the open end width of the horizontal V-shaped pairs is set at about 2-fold of the thickness of the filter cassettes.

Hayashi et al. (Toray Indus., Inc., Japan) [105], observed that the filtering material for chemical filters consists of IEFs and powdered ion exchangers having reversed polarity of the IEFs. The weight ratio of IEFs/powdered ion exchangers is in the range of 1/1-10/1. The IEFs contain PS-type polymeric fibres as base materials. The IEFs are cation exchange fibres, and the powdered ion exchangers are anion exchangers. The filtering material contains thermally fusible materials, e.g., thermal fusible fibres. The filtering material can be filter paper formed by papermaking.

The filters used for waste gas treatment by acidic or alkaline solution has aqueous solution as adsorbent or fibrous ion exchanger filter [106] at the gas outlet. The ion exchange filter removes acid/alkaline mist from the treated gas. Sugo et al., at Japan Atomic Energy Res. Inst., Ebara Mfg., Japan, used ion exchanger fiber-based antibacterial air filters [107] consisting the IEFs of chloromethyl styrene graft polymer quaternary ammonium compounds and 4-vinyl pyridine graft polymer quaternary ammonium compounds. These filters rapidly and certainly collect micro-organisms floating in air and are suitable for use in air conditioning systems.

The ion exchange filter materials have also been prepared in Russia [108] from modified fibrous substrates such as polymethacrylic acid hydrazide. Polymethacrylic acid hydrazide is manufactured by heating poly Me methacrylate in solution with hydrazine or hydrazine hydrate. The reaction is carried out on the surface of a fibrous substrate preimpregnated with Me methacrylate and subsequently polymerized using laser radiation with 70-500 mW/m^{2}S irradiation energy. The fibrous substrate is polyamide, PAN and polyester fabric. This method is used to increase acid resistance, permeability and exchange capacity of filtering medium made of modified fibrous substrate. Filters (e.g. polyesters) containing 10-50% ion exchange fibres [109] are ion exchanged as salts, woven and regenerated at low temperature to the original ion exchange groups to give the fabric capable of removing ionic substances.

Non-woven fabric filter [110] was obtained in Japan, by mixing ion exchange fibres (e.g., cation or anion-exchange fibres) and low m.p. binder fibres (e.g., polyester and PP fibres) to form raw material fibres. These filters can be used for removal of cations (e.g., Na^+, NH_4^+) anions (e.g., F^-, SO_4^{2-}, Cl^-) dust etc.

The air filters consist of an air permeable flat or, 3-dimensional support on which a layer of ion exchange spheres are fixed [111]. By using fabric support, the ion exchange spheres can be placed on one or both sides. The spent filter can be easily regenerated by a hot air flow. This type of filter is suitable for removal of gaseous acid substances (e.g., HCHO, SO_2) and gaseous basic substances (e.g., NH_3). The filter media for air filters contains an unwoven paper or cloth containing a cellulose filament and an ion exchange resin having $\geq$1 absorber (e.g., zeolites, activated carbon, Cu) [112].

Fujiwara et al.. (Ebara Corporation, Japan) used the method and apparatus [113] for removal of tobacco smoke and tobacco odor from air. This includes passing tobacco smoke and tobacco odor containing air through a fibre layer without IEFs and an IEF layer containing strongly acidic cation exchange fibres in order. The apparatus contains air admission part, an adsorption section having the above stated fibre layers and a suction fan. A tobacco smoke sensor is arranged in the vicinity of the air admission part.

Kato et al., at Toshiba Plant kensetsu Co. Ltd., Japan, developed dry scrubbers by using IEFs [114-115]. The dry scrubber is used for removing

ionic substances from waste gases of chemical plants. It is packed with IEF filter which is highly effective for NH_3 & HF removal from waste gases. The savings of electrical energy and water consumption are 33 and 98% respectively, as compared to the conventional wet scrubbers.

The fibrous ion exchanger mats are also used as air filters in continuous ion exchange process [116]. In this process, ≥ 1 liquid batches are forced under pressure through the bed during the stationary stage of the discontinuously rotating ion exchanger mat to effectively carryout the exchange without affecting the continuous functions, e.g., regeneration, charging and flushing of the mats in the various stages of the process by pressing the liquid from the ion exchanger mat, the amount of solution distilled.

The fibrous ion exchangers manufactured by graft polymerization and polycondensation from copolymers, or mixtures of polymers or copolymers and polymer analogous transformation are used in the environmental protection by the sorption of gases [117]. Ionex fibres [118] were discussed in detail for cleaning technology of environment. Thus, the IEFs are used effectively for pollution control [119-120] and are recently investigated to fulfill the role of adsorbent for metal cyanides, especially when these species are presentation low concentration in slurry streams. In this study, relatively low concentration (10 ppm) of Au, Ag, Cu(II) cyanides were adsorbed onto activated carbon, ion exchange membranes and IEF. IEF such as natural activated carbon, PAN,

polytetra fluoro-ethylene, polybenzimidazole and PP are also used as adsorbent especially for Au recovery [121].

The polymeric fibrous ion exchangers are used in the multilayered (7-layer) apparatus [122] which are used for disinfection and purification of water including a multilayered column of material having a strongly basic ion exchanger and a mixed layer of a Ag loaded adsorbent and C-adsorbent (area – 1100m^2/g, pore vol. 0.4 cm^3/g, granules – 0.3-1 mm or fibres 500 g/m^2). Thus, the apparatus for production of pure water [123] includes fibrous filtering material as the impurity removing device.

The IEFs are used in the separation of rare earth metals [124]. The sorption capacity of Cu, Pb, Zn, Fe, Cd, Co, Ni, Hg, Ag, Cr & Mn of various fibrous ion exchangers and C-fibres have been developed [125] under static conditions at various pH values PAN-PEPA, PAN-TTO-MKKhK are found very effective in the removal of heavy metal ions from wastewater. They can easily be regenerated to yield concentrated solution of the metals.

Wen et al. [126] used a new ion exchange chelating fibre with amino. phosphoric and dithiocar bamate groups based on PAN for preconcentration of Be, Bi, Co, Ga, Ag, Pb, Cd, Cu, Mn & In in sea water. The separation of analytes can be achieved from seawater with a concentration factor of at least 200. The method was applied for the determination of trace elements in coastal seawater. The sorption of Fe^{3+}, Cr^{3+}, Cu^{2+}, Cd^{2+} Ni^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}, As^{3-}, As^{5+} and SO_2 by PAN-based fibrous ion exchangers [127-128] containing

primary, secondary and tertiary amino and carboxylic groups were also carried out and the sorption isotherms at different pH of the solution were presented. Thus, these are used [129] as a high efficiency sorbent for metal separation and in water and air purification. Nitron based fibrous sorbents, i.e., AN-1 and Kopan-10, Kapon-60, Kopan-90, Kopan-150, Karpan and Ampan polyampholytes are highly effective in removing Cr, Cd, Zn & Cu ion from electroplating wash waters [130].

Fritz et al. [131] used a functionlized macroporous poly (styrene divinyl benzene) particles in a packed column, or in a non-woven web or fibrous matrix for separations especially for drugs, explosives, pesticides etc.

Polystyrene-based fibrous ion exchangers (especially Ionex series) are used for water purification in nuclear plants [132]. The fibrous ion exchangers are also used in solidification of radioactive wastes [133]. In this process, the waste in placed in a mixing tank, a hydraulic cement- type solidifying agent is injected into the tank along with fibrous material which adsorbs, on its surface. radioactive nuclides in ionic or molecular state, H_2O is added to the materials in the tank, and mixed with them, and the mixture is injected into a container and solidified.

Komatsu, Yu (Natl. Inst. Res. Inorg Mater. Tsukuba, Japan) [134] synthesized layered dihydrogen tetratitanate hydrate fibres which are used for the separation of uranium ions from seawater and for that of Co ions from

cooling water of nuclear reactor for electrical generation. The alkali metals and alkaline earth metals are easily separated by using a column of these fibres.

The cationic exchange fibre non-woven fabrics with uniform fibre distribution and thickness were prepared at Sumitomo Chemical Co. Ltd.. Japan [135] which are useful for water treatment, air purification, gas adsorption etc. They were prepared by contacting aq. dispersion of the regeneration type cationic exchange fibres with an amino alcohol, then filtering to form paper-like sheets. The IEF non-woven fabrics, as a new-unit type harmful gas purifier has been developed [136].

Thus, the IEFs are used for removal of harmful substances [137]. For that, the gases or solutions are treated through IEF adsorption layers for adsorptive removal of harmful substances.

Liu et al. used IEF for removal of arsenate from waste water [138]. The fibrous sorbent have high sorption capacity and good kinetic property for arsenate ions. The removal of arsenate by the fibre reached a maximum in pH value range of 3.5 to 7.0. The column performance was carried out to assess the applicability of the IEF for the removal of arsenate ions with satisfactory result. Diluted NaOH solution is an efficient eluant for the desorption of assenate from the fibre column, and 30 mL of 0.5 $molL^{-1}$ NaOH can quantitatively recover arsenate from water. The IEFs are also used for the recovery of highpurity zinc oxide from steel-making dust [139].

In these laboratories, some fibrous ion exchangers have been synthesized which show promising ion exchange behaviour [140-142]. These exchangers were prepared by the combination of organic polymeric species such as, polystyrene, polyacrylonitrile, acrylamide etc with polybasic inorganic acid salts. The product materials possess better ion exchanger characteristics, mechanical strength and stability than their inorganic counterparts. They have been characterized by some physicochemical methods such as IR, SEM, DTA-TGA etc. in addition to their ion exchange and adsorption behaviour. These materials were found useful in the separation of metal ions. Thus, they are of great importance in industrial and environmental applications.

Surface chemistry [143] is the study of structures, functions, and phenomena of the surfaces. It involves the observation and measurement of forces acting at the surfaces of gases, liquids and solids or at the interface between them. Dissolution and crystallization, electrode processes, heterogeneous catalyses, corrosion, emulsions (liq/liq interfaces), adsorption catalysis, vapour pressure solubility (surface tension of liquids) and many other important phenomena take place at interfaces. Therefore, the subject of surface chemistry is of great importance not only from the academic point of view but also from the point of view of the applied chemistry.

The theory of surfactant behaviour is now an extensive branch of surface chemistry and considerable basic research has been carried out in the last 20 years. The major reason for this work is the possible shortage of oil in the

1970s leading to the use of surfactants in enhanced oil recovery. Now, the importance of the physical chemistry of surfactant behaviour is being recognized in biochemistry. A feature impetus to surfactant research has been the development of thin film technology in the production of microelectronics by the use of Langmuir-Blodgett films.

Surfactants constitute the most important of detergent components. '*Surfactant*' is an abbreviation for *surface-active agent,* which literally means "*active at the surface*". The surface can be between solid and liquid, between air and liquid, or between a liquid and a different immiscible liquid.

Surfactants, surface-active agents or detergents are amphiphilic, organic or organomentallic compounds which form association colloids or micelles in solution. Amphiphilic substances or amphiphiles comprised of a hydrophobic portion, usually a long alkyl chain, attached to hydrophilic or water solubility enhancing functional groups. Actually, surfactant molecule consists of 2 parts: a water hating (hydrophobic) part and a water loving (hydrophilic) part. Fig.1.3 shows the basic structure of surfactant molecule.

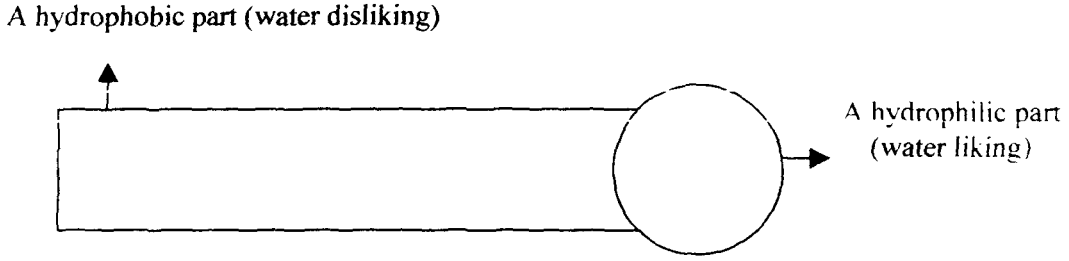


Fig. 1.3 Basic structure of surfactant molecule

Surface active agents are often called by other names including surfactants (particularly in the USA), association colloids, colloidal

electrolytes, paraffin chain salts, amphitpathic compounds, heteropolar tensides (particulary in Europe). It should be noted, however, that whereas most detergents (from the Latin, *detergene* – cleansing) are surface active agents, but not all surfactants, surface active agents are detergents [144].

Surfactants are compounds that reduce surface tension when dissolved in water or water solutions or which reduce interfacial tension between 2 liquids, or between a liquid and a solid [145-146]. When a surfactant molecule is introduced into water, the water hating part tries to escape by attaching itself to any available surface other than water. At the same time the water-loving part tries to remain in water. As a result, surfactants tend to strongly "*adsorb*" or cling to many surfaces, such as fabric, soil, glass and where the water and air meet (the water/air interface).

- When they adsorb to a surface, surfactants can loosen and remove the soils from the surface.

- When the adsorb to soil, surfactants hold soil particles in suspension and help prevent them from redepositing onto the surface from which they have been removed.

- When they are adsorbed at the water/air interface, they reduce the surface tension of water and allow the water to spread out. Without the use of a surfactant, water tends to "bead-up" in droplets. This beading slows down the wetting of the surface and inhibits the cleaning process.

Surfactants make water "*wetter*". Thus, functionally, surfactants are of 3 categories: detergents, wetting agents and emulsifiers: all have the basic chemical mechanism and differ chiefly in the nature of the surface involved.

Depending on the chemical structure of the hydrophobic moiety bound to the hydrophobic portion, the surfactant may be categorised into 4 types:

- Anionic surfactant
- Cationic surfactants
- Non-ionic surfactants
- Ampholytic surfactants, or (zwitter ionic)

(1) Anionic surfactants: Anionic surfactants are [147-148] those in which the negative ion is surface active. The most frequently used anionic surfactants are alkali or alkaline earth metal salts of mono or polybasic carboxylic (fatty) acids and of sulfuric, sulfonic & phosphoric acids containing a saturated or unsaturated hydrocarbon substituent

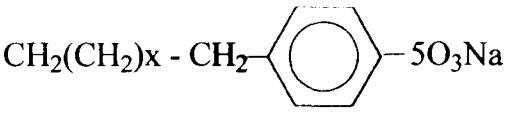
For e.g.

$CH_3(CH_2)_x\ CH_2O–SO_3Na$

Linear Alkyl Sulfates (LAS)

$CH_3(CH_2)_x\ CH_2O–SO_3Na$

Linear Alkyl Sulfonates (LAS)



Linear Alkyl benzene sulfonates (LABS or ABS)

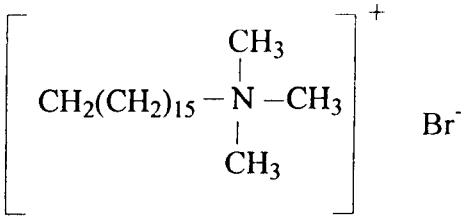
$R–C_2H_4O–OSO_3M$

Alklyl ethoxy sulfates (AES)'

Table 1.2 shows some anionic surfactants with their chemical formulas. Anionic surfactants are effective in removing particulate (dirt, dust etc) and oily soils. In hard water, they react with positively charged water hardness minerals, such as calcium and magnesium. Soap is the original anionic surfactant. In hard water, it combines with Ca^{++} & Mg^{++} salts to form an insoluble soap film or scum. In general, anionic surfactants tend to generate higher suds levels than other classes of surfactants.

(2) Cationic surfactants: Cationic surfactants are those [149] in which the positive ion is surface active. They have the general formula of $R_n X^+ Y^-$, where R, represents one or more hydrophobic chains, X is an element capable of forming an 'onium' structures, and Y, is the counter ion. Cationic surfactants are usually quaternary ammonium salts, $R_4N^+X^-$.

For e.g.,



Cetyl trimethyl ammonium bromide (CTAB)

$C_{12}H_{25}N^{+}(CH_3)_3Cl^{-}$

Dodecyl trimethyl amm. Chloride (DTMAC)

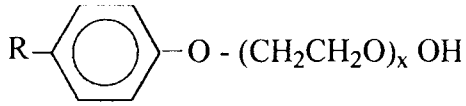
Table 1.3 shows some cationic surfactants with their chemical formulas. Cationic surfactants can be used as effective antimicrobial agents in hard surface cleaners.

(3) Non-ionic surfactants: Non-ionic surfactants are those [150-151] in which the whole molecule is surface active. They do not have an electrical charge. Most nonionic surfactants are polyoxyethylene and polyoxypropylene derivatives (of compounds such as alkyl phenols and alcohols, fatty acids esters, and alkyl amines, amides and mercaptans) or, polyalcohols, carbohydrate esters, fatty alkanol amides and fatty amine oxides.

For e.g.,

CH_3–$(CH_2)_x$ – $(C_2H_4O)_y$–OH [X = 7-19, y = 12]

Linear alkyl ethoxylates (LAE)

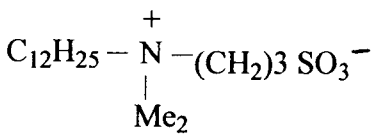


Alkyl phenol ethoxylates (APE)

Table 1.4 shows some nonionic surfactants with their chemical formulas. Because of absence of electrical charge, they tend to be less seriously affected by H_2O hardness. In general, they are low foaming and are especially useful in products which are designed to require little rinsing.

(4) Ampholytic (Zwitter ionic) Surfactants: The ampholytic surfactants are those in which there are more than one surface active species in a molecule. It means they possess both anionic and cationic groups on the hydrophobic moiety. Depending on the pH of the solution and the structure, they can behave as either an anionic, cationic or neutral species.

For e.g.,



3,3-dimethyl dodecylamine propare sulfonate

Table 1.5 shows the some ampholytic surfactants with their chemical formulas.

Table 1.2: Some Anionic Surfactants

Surfactant	Structure/Chemical Formula
Heptafluorobutyric acid	$CF_3(CF_2)_2\ COOH$
Sodium decyl sulfate	$CH_3(CH_2)_9SO_4^-Na^+$
Sodium decyl sulfonate	$CH_3(CH_2)_9SO_3^-Na^+$
Cobalt dodecanoate	$[CH_3(CH_2)_{10}COO^-]_2\ Co^{2+}$
Aluminium dodecyl sulfate	$[CH_3(CH_2)_{11}SO_4^-]_3\ Al^{3+}$
Copper (II) dodecyl sulfate	$[CH_3(CH_2)_{11}SO_4^-]_2\ Cu^{2+}$
Potassium dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^-K^+$
Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4^-Na^+$
Sodium dodecyl sulfonate	$CH_3(CH_2)_{11}SO_3^-Na^+$
Sodium p-dodecyl sulfonate (SDBS)	$p\text{-}CH_3(CH_2)_{11}\ C_6H_4SO_3^-Na^+$
Sodium hexadecanoate	$CH_3(CH_2)_{14}COO^-Na^+$
Potassium hexadecyl sulfate	$CH_3(CH_2)_{15}SO_4^-K^+$
Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7\ COO^-Na^+$
Sodium oleyl sulfate	$CH_3(CH_2)_7CH{=}CH(CH_2)_8\ SO_4^-Na^+$
Potassium dodecanoate	$CH_3(CH_2)_{10}COO^-K^+$

Table 1.3: Some cationic surfactants

Surfactant	Structure/Chemical formula
Decyl amm. Bromide	$CH_3(CH_2)_9N^+H_3Br^-$
Decylmethyl amm. Bromide	$CH_3(CH_2)_9N^+H_2\,CH_3Br^-$
Decyldimethyl amm. Bromide	$CH_3(CH_2)_9N^+H(CH_3)_2\,Br^-$
Dodecyl ammonium Chloride	$CH_3(CH_2)_{11}N^+H_3\,Cl^-$
Decyltrimethyl amm. Bromide	$CH_3(CH_2)_9N^+(CH_3)_3\,Br^-$
Dodecyltrimethyl amm. Nitrate	$CH_3(CH_2)_9N^+(CH_3)_3\,NO_3^-$
Dodecyltrimethyl amm. Chloride	$CH_3(CH_2)_9N^+(CH_3)_3\,Cl^-$
1-Dodecyl pyridinium chloride	$CH_3(CH_2)_{11}N^+C_5H_5\,Cl^-$
1-Dodecyl pyridinium iodide	$CH_3(CH_2)_{11}N^+C_5H_5\,I^-$
Dodecyl benzyl dimethyl amm. Chloride	$CH_3(CH_2)_{11}C_6H_4CH_2N^+\,(CH_3)_2\,Cl^-$

Table 1.4: Some Nonionic surfactants

Surfactant	Structure/Chemical formula
Polyoxyethylene (3) decanol	$CH_3(CH_2)_9O\,(CH_2CH_2O)_3H$
Polyoxyethylene (6) dodecanol	$CH_3(CH_2)_{11}O\,(CH_2CH_2O)_6H$
Polyoxyethylene (6) hexadecanol	$CH_3(CH_2)_{15}O\,(CH_2CH_2O)_6H$
Polyoxyethylene (6), 8,8,8-tri fluoro-octanol	$CF_3(CH_2)_7O\,(CH_2CH_2O)_6H$

Polyoxyethylene (8) dodecanol	$CH_3(CH_2)_{11}O\ (CH_2CH_2O)_8H$
Polyoxyethylene (9) hexadecanol	$CH_3(CH_2)_{15}O\ (CH_2CH_2O)_9H$
n-Octyl sulfinyl ethanol	$CH_3(CH_2)_7SO\ CH_2CH_2OH$
8,8,8-trifluoro-octyl methyl sulfoxide	$CF_3(CH_2)_7\ SOCH_3$
N.N-Dimethyl dodecyl amine oxide	$CH_3(CH_2)_{11}N(CH_3)_2$ $\downarrow$ O

Table 1.5: Some Zwitterionic Surfactants

Surfactant	**Structure/Chemical formula**
3-(Dimethyl dodecyl ammonio)-propane-1-sulfonate	$CH_3(CH_2)_{11}N^+\ (CH_3)_2(CH_2)_3SO_3^-$
3-(Dodecylmethyl ammonio)-propane-1-sulfonate	$CH_3(CH_2)_{11}N^+H\ CH_3(CH_2)_3SO_3^-$
3-(Dimethyl hexadecyl ammonio)-propane-1-sulfonate	$CH_3(CH_2)_{15}N^+\ (CH_3)_2\ (CH_3)_3\ SO_3^-$
N-Dodecyl-N,N-dimethyl glycine	$CH_3(CH_2)_{11}N^+(CH_3)_2\ CH_2\ COO^-$
C-Dodecyl-N,N-dimethyl glycine	$CH_3(CH_2)_{11}CHN^+(CH_3)_3$ $\vert$ COO^-
N-Dodecyl-3-amino propionic acid	$CH_3(CH_2)_{11}N^+H_2\ CH_2CH_2\ COO^-$
N-Dodecyl-amino benzyl phosphinic acid	$CH_3(CH_2)_{11}N^+H_2CH(C_6H_5CH_2)PO_2^-H$

Adsorption and CMC

There are 3 basic concepts which need to be well understood in order to explain the majority of observed phenomena; these are *solubility, adsorption of a surfactant at a surface*, and the *formation of micelles* in solution. These 3 phenomena differentiate a surfactant from other chemical entitities. It is the abnormal solubility characteristics of surfactants that give adsorption, and form micelles. It is the adsorption at the surfaces that gives the surface active effect of foaming, wetting, emulsification, dispersing of solids and detergency. It is the miceller properties that give the solution and bulk properties of surfactants such as viscosity and solubilisation, but also there is increasing evidence that the micellar properties are necessary in functional effects such as emulsification and detergency.

They unique property of surfactants is that the *higher concentration at the surface* than in the bulk of a liquid. This phenomenon is known as "*adsorption*" and occurs at a *liquid/ solid, liquid/liquid and at a air/liquid interface* which is shown in Fig.1.4. Solubility of the materials ensures that a reservoir of surface active agent is available to accommodate the large surface area of the various interfaces encountered in practical applications.

In dilute aqueous solution, generally less than 10^{-4} M, the behaviour of ionic surfactants parallels that of strong electrolytes while the behaviour of nonionic surfactants often resembles that of the simple organic molecules. At higher surfactant, concentrations, however, a pronounced deviation from

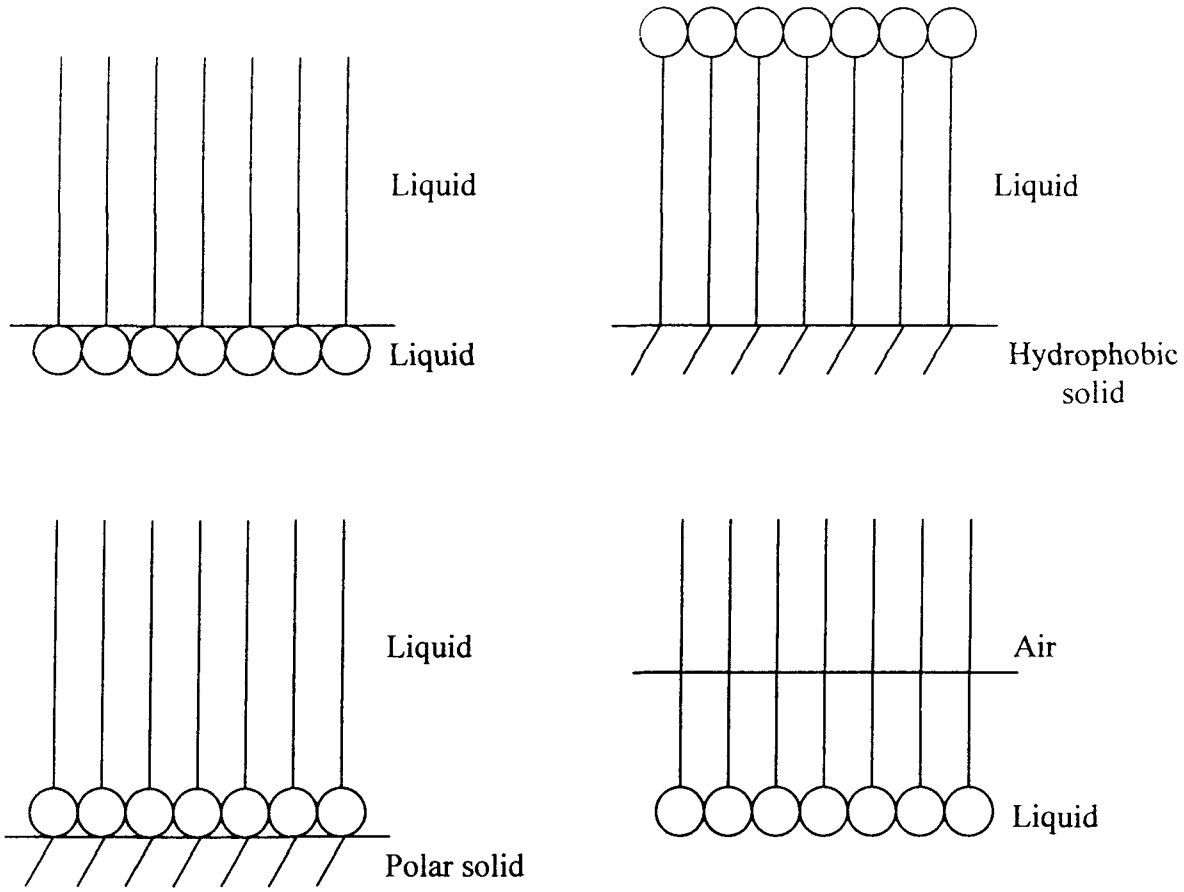


Fig.1.4 Adsorption of surfactant at interfaces

"ideal" behaviour in dilute solution occurs this deviation generally being considerably larger than that exhibited by simple strong electrolytes. Thus, the adsorption of a surfactant from solution onto a surface depends upon the concentration and Fig.1.5 shows the effect of increasing concentration [152]. At very low concentration (I, II), the molecules lies flat on the surface. As the concentration increase at (III), the surfactant molecules begin to orient and at the concentration (IV), the surfactant molecules form monolayer, this particular concentration is of importance and known as the *critical micelle concentration (CMC)*. At concentration (V), above the CMC the surfactant molecules form an ordered structure, known as "*micelle*".

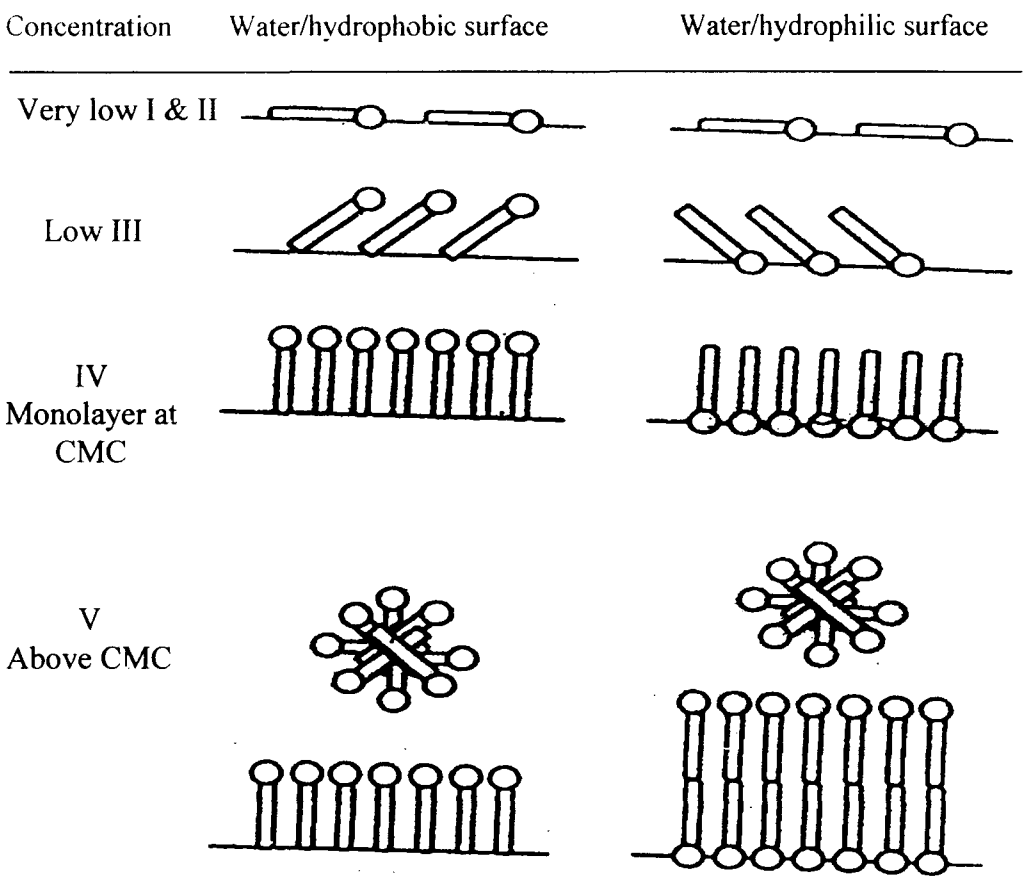


Fig. 1.5 Adsorption and concentration

Thus, the narrow range of concentration which the micelles first become detectable is the critical micelle concentration, CMC. A more formal definition of the CMC is that concentration of the surfactant at which the concentration of the micelles would become zero if it were to continue to decrease as it does at a slightly higher concentration (Williams et al., 1955).

The different experimental methods available for determining the CMC are summarized by Shinoda et al. (1963) and Elworthy et al. (1968) and are discussed critically by Mukerjee & Mysels (1971).

Each surfactant has a characteristic CMC value. The most obvious evidence of miceller growth is probably the dramatic increase in viscosity with increasing concentration which is observed in several surfactant solutions. Micellar growth is favoured by decreasing the temperature, adding electrolyte and lengthening the surfactant chain length and is, furthermore, very sensitive to the nature of the counter ion.

Depending upon the chemical structure of the surfactant, its micelle can be cationic, anionic, zwitterionic, or nonionic. The electrostratic character of the micelles depends in some cases, on the pH of the aqueous solution due to protonation equilibria. Zwitterionic surfactants, of course, also can become either cationic or anionic, and several types of nonionic surfactants can also form anioninc or cationic micelles in the appropriate pH range. Micelles are not static species but rather exist in a dynamic equilibrium. The kinetics of micelle dissociation have been measured for several surfactants by stopped flow (Jaycock and Ottewill, 1967; Lang et al., 1972; Yasunaga et al., 1973), temperature jump (Kresheck et al., 1966; Bennion et al., 1969; Bennion and Eyring, 1970; Lang & Eyring, 1972; Takeda & Yasunaga, 1973), pressure jump (Takeda & Yasunaga, 1972; 1973; Janjic & Hoffmann, 1973; Hermann &^ Kahlweit, 1973) and ultrasonic relaxation techniques (Yasunaga et al.., 1967; Graber & Zana, 1970; Graber et al.., 1970; Sams et al.., 1972; Lee 1973 ; Adair et al., 1974; Rassing et al., 1973, 1974).

The micelle may be represented as a globular, cylindrical or ellipsoidal cluster [153] of individual surfactant molecules in equilibrium with its monomer [154-155]. The reverse orientation of the hydrophilic & hydrophobic part of the surfactant in a hydrocarbon medium leads to reversed micelles [156]. Fig. 1.6 shows the shapes of micelles and Fig. 1.7 shows the 2-dimensional schematic representation of the regions of a spherical ionic micelles.

Since the alkyl chain length of a surfactant has a decisive influence on its physiochemical properties and hence on various biochemical applications [157], each surfactant has been analysed w.r.t. the uniformity of the alkyl chain by various techniques such as TLC, HPLC, GC (after hydrolysis), some traditional surfactants, such as the Triton-series, are mixtures of a variety homologues and must correspond to the standard mixture. Surfactants consisting of only one species are characterized by a minimum purity assay which refers to the chain homologue purity. Each surfactant is further checked for appearance, solubility, identity (by FTIR and/or NMR) and relevant trace impurities such as the respective starting material, peroxides UV-absorbing foreign materials and metal traces by ICP-AES. The stereochemical purity is checked by measuring optical rotation.

The surfactants are of widespread importance in the detergent industry, in emulisification, lubrication, catalysis, tertiary oil recovery, and in drug delivery.

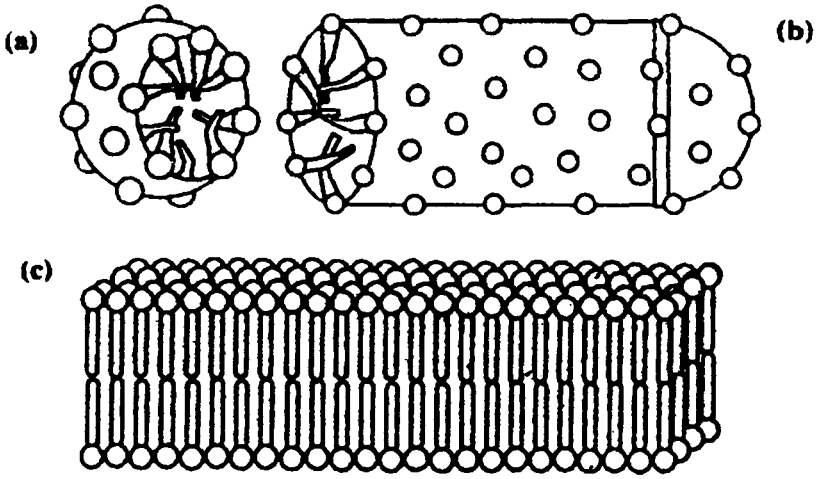


Fig.1.6 Shape of micelles: (a) spherical; (b) rod-shaped or cylindrical; (c) lamellar.

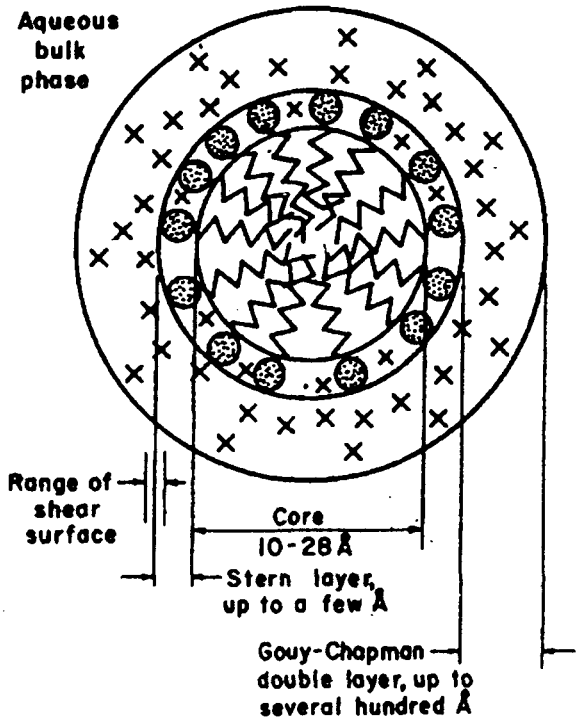


Fig.1.7 A two-dimensional schematic representation of the regions of a spherical ionic micelle. The counterions (X), the head group (O), and the hydrocarbon chain (^^^) are schematically indicated to denote their relative locations but not their number, distribution, or configuration.

In analytical chemistry, surfactants have been recognized as being very useful for improving analytical technology, e.g., in chromatography [158] and luminescence spectroscopy [159-160]. The use of surfactants in chromatography particularly in ion exchange is of our interest. It is well-known that surfactants are composed of 2 parts – hydrophobic and hydrophilic, which are oppositely charged, and the surfactants also act as ion exchangers. When their solution are in contact with solid material, they adsorb on the surface remaining their hydrophilic part in aqueous solution due to their surface-active property and they make that surface "active".

As it is clear form the above, fibrous ion exchangers have a great utility in environmental studies, particularly in industrial applications. They have a great scope in future also, further, the surfactants play an important role in the adsorption behaviour of the substances. Since they are the materials possessing ion exchange characteristics also, it should be interesting to see how they can alter the ion exchange behaviour of a material when present in the aqueous systems. Our preliminary work points to the fact that they have a significant contribution in this regard and alter then adsorption characteristics of the adsorbents. To elaborate it further and to have a greater insight of the mechanism undergoing the process it was found worth while to study in detail *the effect of surfactants on the adsorption behaviour of the ion exchange materials* for the heavy metal ions present in aqueous media. The following chapters summarize our efforts in this direction. We have selected *n-butyl*

acetate based Cerium (IV) phosphate and *Sn (IV) phosphate* as the basic ion exchangers which have been synthesized in the fibrous and non-fibrous forms. respectively, adopting the methods given in chapter-2. These materials have been subjected to a detailed study for their adsorption behaviour for some metal ions important from the pollution point of view in the presence and absence of the surfactants to draw certain conclusions. This part of the study is summarized in chapter – 3.

REFERENCES

1. L. S. Ettre, "Nomenclature for Chromatography", Pure and Appl. Chem. 65(4) (1993) 819.

2. Qureshi, Saidul Zafar; Ahmad, Syed Taufeeq; Rahman, Nafisur (Dep. Chem., Aligarh Muslim University, Aligarh, India), Chem Anal. (Warsaw) 1992, 37 (1), 21-4 (Eng.).

3. The Second Book of Moses, Exodus, Chap, 15, Verse 25.

4. Aristotle, works about 330 BC, Clarenndon Press London, 7 (1927) 933 b.

5. H.S. Thompson and J. Roy, Agr. Soc. Engl., 11 (1850) 68.

6. J.T. Way and J. Roy, Agr. Soc. Engl., 11 (1850) 313.

7. H. Eichorn, Ann. Physik. Chem., 105 (1858) 126.

8. F. Harms and A. Rumpler, 5th Inter. Congr. Pure Appl. Chem., 50 (1903).

9. O. Follin and R. Bell, J. Biol. Chem., 29 (1917) 329.

10. R. Gans, Jahrb. Preuss. Geol. Landesanstalt (Berlin), 26 (1905) 179.

11. B.A. Adams and E.L. Holms, J. Soc. Chem. Ind., 54 (1935) 11.

12. K.g. Varshney, "New Developments in ion exchange" Proceedings of the international conference on ion exchange, ICIE, 91, Tokyo, Japan (1991), 413.

13. C.B. Amphlett, Inorganic Ion Exchangers, Elsvier, Amsterdam (1964).

14. M.J. Fuller, Chromatogr. Rev., 14 (1971) 45.

15. M. Qureshi, S.A. Nabi, J.P. Gupta and H.S. Rathore, Sep. Sci., 7 (1972) 615.

16. V. Vesely and V. Pekarek, Talanta, 19 (1972) 219, 1245.

17. A. Clarfied, I and EC Research, 34 (1995) 2865.

18. A. Clearfield, Chem. Rev. 88 (1998) 125.

19. G. Alberti, M. Casciola and U. Costantino, J. Membr. Sci. 16 (1983) 137.

20. G. alberti, and U. Costantino, J. Chromato., 102 (1974) 5.

21. K. G.Varshney and Ali Mohammad, Chem. and Environ. Research, 1 (1992) 353.

22. A. Clearfield Ed., Inorganic Ion Exchange Materials, CRC Press, Inc. Boca Raton, Florida (1982).

23. M. Qureshi and K.G. Varshney Eds., Inorganic ion Exchangers in Chemical Analysis, CRC Press, Inc. Boca Raton Florida (1991).

24. A. Dyer, An Introduction to Zeolite Molecular Sieves, Bath Press Ltd., Avon (1988).

25. A. Dyer and R.P. Townsend, J. Inorg. Nucl. Chem., 35 (1973) 3001.

26. M. Qureshi and K.G. Varshney, J. Inorg Nucl Chem., 30 (1968) 3081.

27. M. Qureshi, K.G. Varshney and F. Khan, Sepn. Sci., 6 (1971) 559.

28. M. Qureshi, K.G. Varshney and A.H. Israili, J. Chromatogr., 59 (1972) 141.

29. M. Qureshi, K.G. Varshney and F. Khan, J. Chromatogr., 65 (1972) 547.

30. M. Qureshi, K.G. Varshney and S.K. Kabiruddin, Canad. J. Chem., 50 (1972) 2071.

31. M. Qureshi, K.G. Varshney and F. Khan, Sepn. Sci., 8 (1973) 279.

32. M. Qureshi, K.G. Varshney and N. Fatima, Sepn. Sci and Techn., 13 (1978) 321.

33. M. Qureshi, K.G. Varshney and S.D. Sharma, Sepn. Sci. and Techn. 13 (1978) 917.

34. K.G. Varshney, A.A. Khan and A.R. Khan, Bull. Chem. Soc. Jpn. 61 (1988) 3693.

35. K.G. Varshney and S.M. Maheshwari, Ecotox. Environ. Safety, *18* (1989) 1.

36. K.G. Varshney, U. Sharma and S. Rani, J. Ind. Chem. Soc., 61 (1984) 220.

37. K.G. Varshney, S. Agrawal, K. Varshney, A. Premadas, M.S. Rathi and P.P. Khanna, Talanta, 30 (1983) 955.

38. K.G. Varshney, S. Agrawal and K. Varsheny, Sepn. Sci. and Tech., 18 (1983) 59.

39. K. G. Varshney, S. Agrawal and K. Varshney, J. Liq. Chromatogr., 6 (1983) 1533.

40. K.G. Varshney, S. Agrawal and K. Varshney, Analyt. Lett., 16 (1983) 685.

41. K.G. Varshney, S. Agrawal, K. Varshney and V. Saxena, Analyt. Lett., 17 (1984) 2111.

42. K.G. Varshney, S. Agrawal and K. Varshney, Analyt. Lett., 16 (1983) 1381.

43. K.G. Varshney, S. Rani, S. Anwar and U. Sharma, Analyt. Lett., 18 (1985) 2033.

44. K.G. Varshney, S. Rani and R.P. Singh, Ecotox Environ. Safety, 11 (1986) 179.

45. W.V. Malik, S.K. Shrivastava & S. Kumar, Talanta, 23 (1976) 323.

46. R.B. Chetverina, E.S. Biochinova, Zh. Prikl. Khim. 50 (1977) 1181.

47. R.B. Chetverina. E.S. Biochinova. Ibid., 50 (1977) 1183.

48. K.G. Varshney, Altaf Hussain Pandith, Chem. Environ. Res., 5 (1-4) (1996) 141-154 (Eng.).

49. Ram Niwas, A.A. Khan, K.G. Varshney Colloids and Surf. A: Physicohem. Eng. Aspects, 150 (1999) 7-14.

50. P. Bajaj, S.K. Munukutla, Text Res. J. 60 (1990) 113.

51. P. Bajaj, D.K. Paliwal, Indian J. Fibre Text Res. 16 (1991) 89.

52. M.H. Kotze, F.L.D. Cloete, Ion Exch. Adv., Proc. IEX 92 (1992) 366.

53. P. Bajaj, M. Goyal, R.B. Chavan, J. Appl. Polym. Sci. 51 (1994) 423.

54. M.P. Zverew, Chemisorptive Fibres, Khimiya, Moscow, (1981) 191 (in Russian).

55. L.A. Wolf, Fibres of Specific Properties, Khimiya, Moscow (1980) 240.

56. L.A. Wolf, Chem. Ind. (Bulgaria) 3 (1983) 134.

57. T. Miyamatsu, Sen'i Gabbaishi 39 (1983) 53.

58. A.I. Vulikh, Alovyajuikov and G.A. Nikandrov, Gas Purification as a New Scope of Ion Exchanger in M.M. Senjavin (Ed.), Ion Exchange. Nauka, Moscow (1981) 214.

59. K. Sugasaka and S. Katoh, Sepn. Sci. and Tech., 16 (1981) 971.

60. K. Saito and S. Furusaki, J. Nucl. Sci. Tech., 20 (1983) 352.

61. F. Vemon and T. Shah, React. Polym. 1 (1983) 301.

62. Certificate for the "Fiban" trademark No. 77959, 25.02.1985, USSR.

63. V.S. Soldatov, A.I. Pokrovskaya and R.V. Martsinkevich, J. Appl. Chem. USSR, 9 (1984) 2030.

64. V.S. Soldatov, R.V. Martsinkevich and A.I. Pokrovskaya, J. Appl. Chem. USSR, 57 (1984) 1410.

65. V.S. Soldatov, G.I. Sergeev, R.V. Martsinkevich, A.I. Pokrovskaya, A.A. Shunkevich, Dekl. Alad, nauk BSSR, 28 (1984) 1009.

66. V.S. Solatov, R.V. Martisinkevich, G.I. Sergeev, A.I. Pokrovskaya (Inst. Fiz-org. Khim, Minsk, USSR) Zh. Prikl. Khim (Leningrad) 1989, 62 (7), 1676-9.

67. L.A. Volf, Ed., "Special Fibers", Khimia (in Russian).

68. V.S. Soldatov, A.A. Shunkevich, G.I. Sergeev, Reactive Polymers, (1988) 159.

69. V.S. Soldatov, I.S. Elinson, A.A. Shunkevich in "Chemistry for Protection of the Environment", L. Pawlowaki, G. Alberts, W. Lacy, Eds, pp. 369-386, Elsvier (1986).

70. T. Yoshioka, M. Shimamura, Bull. Chem. Soc. Jpn., 56 (1983).

71. T. Yoshioka, Bull. Chem. Soc. Jpn., 58 (1985) 2618.

72. R.M. Kautzmann, C.H. Sampaio, J.L. Cortina, V. Soldatov, A Shunkevich, [Processing Laboratory (LAPROM), Universidade federal Rio Grande do sul in Porto Alegre, Brazil]. JOM 2002, 54 (10), 47-51 (Eng.), Mineral, Metals and Material Society.

73. Zhou, Lin; Shaoji (Dep Chem. Engg.) Beijing (Inst. Clothing Tech. Pep. Rep. China 1000029). Lizi Jiauohuan Yu Xifu 1993, 9 (6), 486-92 (Ch).

74. Hwang, Tack-Sung; Choi, Jae-Eun; Lee, Jae-Chun (Deptt of Chem. Engg., College of Engg. Chungnam National Univ. Daejon, 305-764 S. Korea). Polymer (Korea) 2002, 26 (1) 121-127 (Korean).

75. Hwang, TackSung; Kim, Kwang Young; Lee, Chun Woo; park, Kil Bok (Ace Lab, Inc. S. Korea) Repub. Korean Kongkae Tacho Kongbo KR 2000 12, 405 (Cl. BOIJ 20/26), 6 Mar 2000.

76. T.V. Orlova, V.E Nemilov, (Sankt-Peterburgskii Gosudarstvennyi Universitet Tekhnologii i Dizayna, Russia) Russ. RU 2, 194, 809 (C. DOIF 11/104), 20 Dec 2002 Appl. 2000, 133, 106, 26 Dec. 2000.

77. I.G. Rumynskaya, E.P. Romonava, I.I. Paptosova, (St. Petersburg, Gos. Univ. Tekhnol. Dizaina, St. Petersburg Russia) Zh. Prikl. Khim St. Petersburg, 1995, 68 (4) (Russia).

78. Barash, Arkadij Naumovich; Kostina, Tatyana Fedorovna, Zverev, Mikhail Petrovich (Nauchno-Priozvodstvennoe Ob'edinenie

"Khimvolokno" Macau) Russ. RU 2,044, 748 (U. CO8J5/22), 27 Sep. 1995.

79. Li, Yi; Yu, Donghong; Liu, Zheng; Zhang, Baowen (Central Iron + Steel Research Inst. Beijing Peop. Rep. China 100081). Yejin Fenxi 2002, 22 (5), 1-5 (Ch).

80. I. Yu Andreeva, L.A. Ponetaikina, E.Ya Danilova, (USSR). Zh. Prikl. Khim. (Leningrad) 1990, 63 (1), 68-71 (Russ.).

81. E.E. Ergozhin, L.N. Prodius, S.E. Ismailova, B. Kapparov, F. Kh. Shakhabudinova, K. Kh Tastanov (Institute of Chemical Sciences, Academy of Sciences, Kazakh S.S.R.; "Kazlegprom" Scientific Industrial Enterprises) USSR SU 1,705,310 (Cl CO8J5/20), 15 Jan. 1992.

82. L. Yu. Novoselova, V.V. Bordunov (Inst. Khim. Nefti, SORAN, Russia), Plasticheskie Massy 2002 (8), 6-8 (Russ).

83. L. Yu. Novoselova, V.V. Bordunov (Inst. Khim. Nefti, SORAN, Russia). Plasticheskie Massay 2003 (7), 25-27 (Russ).

84. Kato, Koichi; Ito, Yasuhiro; Nakamura, Tatsuo; Tanaka, Masahisa; Yamazaki, Hiroaki (Japan Vilene Co., Ltd., Japan) Jpn. Kokai Tokkyo Koho JP 2002, 294,558 (Cl. DO6M14/28), 9 Oct. 2002.

85. Mogi, Katsumi [Res. Div., Tomoegawa Paper Co., Ltd. Japan) Knobatekku 2003, 31 (11), 66-71 (Japan), Koko Gijutsu Kenkyukai.

86. Hwag, Tack-Sung; Park, Tin-Won; Lee, Iae-Chin [Deptt of Chem. Engg.; College of Engg. Chungue National University Taejon 305-764 S. Korea).

87. L.Yu. Novoselova, V.V. Bordunov, L.I. Vinnichenko (Inst. Khim. Nefti, SORAN Russia). Plasticheskie Massy 2003 (8), 9-10 (Russ).

88. Kotze, H Martha, F.L.D. Clote, (Dep. Metall. Engg. Univ. Stellenbosch, 7600, S. Afr.) Ion Exch. Adv. Proc. IEX 1992, 366-73 (Eng.) Edited by Slater, M.J. Elsivier: London U.K.

89. Hoyori, Masaru; Hirata, Nami,; Yoshika, Toshio (Toray Indus.) Jpn. Kokai Tokkyo Koho JP 0623,282 [9423,282] (Cl BOIJ 47/12), 01 Feb. 1994.

90. T.N. Omelchenko, I.S. Elenson, V.I. Martinovich, V.S. Soldatov. V.I. Tsigankov (Inst. Fiz-Org. Khim, NAN, Belarusi) Vestsi-Nats Akad Navuk Belarusi, Ser. Khim. Navuk 2000, (4) 87-92 (Russ),

91. L. Yu Novoselova (Inst. Khim. Nefti, SORAN Russia). Plasticheskie Massay 2002, (11), 42-44 (Russ).

92. H.M. Zeng, Lu Y; Fu R.W.; W.P. Lin, S.P. Zhu, (Mater. Sci. Inst. Zhongshan Univ. Canton, Peop. Rep. China 510275). Trans. Mater. Res. Scoci. Japan (1994) 18A (Ecomaterials) 656-60 (Eng.)

93. Zeng, Hammin, Lu, Yun (Mater. Sci. Inst. Zhongsham Univ. Canton. Peop. Rep. China 510575) Lizi Jiaoheean Yu Xifu, (1993) 9(5) 464-77 (Ch).

94. D.G. Silchenko, I.N. Illarniov, M.P. Zverev, (Vocnn. Akad. Khim. Zashchity Russia) Khim, Volokna 1995 (2) 15-17 (Russ).

95. E.M. Aizenshtein (USSR). Khim. Volokna 1991, (5), 19-25 (Russ.).

96. Nakayama, Masaaki, Hirata, Nami (Toray Industries Inc., Japan) Jpn Kokai Tokkyo Koho 5P 2000, 19 April. 1999; 4 pp (Jpn).

97. N.V. Smirnova, G.A. Gabrielyan, (Moscow Textile Inst.) USSR SU 1,520,154 (Cl DOI F 11/04), 07 Nov. 1989.

98. K.E. Perepelkin (St. – Peterb. Gos. Univ. Tekhnol Dizaina, St. Petersburg, Russ.). Tekstilnaya Khimiya 2001, (1) 19-31 (Russ).

99. Shudo, Toshiaki, Furukawa, Masahiro, Kuroki, Katsunori (Toshiba Corp.; Kurita Water Industries, Ltd.) Jpn. Kokai Tokkyo Kaho JP 04. 193, 314 [92, 193, 314] (Cl BOID 39/16), 13 Jul 1992.

100. Fujiwara, Goro; Masuda, Mitsunobu; Matsumoto, Shinya; Tsubota, Taiji (Takuma Co. Ltd., Suntory Ltd.; Shinanen New Ceramic K.K.). Jpn. Kokai Tokkyo Koho JP 0422,410 [92, 22, 140] (Cl BOID 39/14), 27 Jan. 1992.

101. Hirata, Nami. Matsumoto, Kazuhiko, Nagase, Motoki (Toray Industries Inc.; Japan) Jpn. Kokai Tokkyo Koho JP 2000, 317, 243, 21 Nov. 2000.

102. Sakata, Kunihiro; Nonaka, Masahiro; Suenaga, Toshinori; Tokunaga, Shingo; Shutoku, Susumu; Fujiwara, Goro; Hattori, Shinji; Irie, Naoki [NEC Kyushu, Ltd.; Takuma K.K., Japan) Jpn. Kokai Tokkyo Koho JP 09, 141, 027 [97, 141, 027] (Cl. BOID 46/10), 3 Jun 1997.

103. Beziris, Janase; Chirica, Mihari (Institul de cercetari si Modernizari Energetice, Bucuresti, Rom). Rom. RO 105, 893 (Cl. BOID 11/00), 30 Jan 1993.

104. Endo, Naotoshi; shima, Hiroyuki; Bessho, Nobuyori; Yamaguchi, Makoto (Ebara Corp. Japan) Jpn. Kokai Tokkyo Koho Jp 09, 220, 426 [97, 220, 426] (Cl BOID 46/52), 26 Aug. 1997.

105. Hayashi, Yuichiro; Fujimura, Yoichi (Toray Industries, Inc. Japan) Jpn. Kokai Tokkyo Koho JP 2002, 292,217 (Cl BOID 39/14), 8 Oct. 2002.

106. Saito, Akuyuki; Unohara, Seetoshi; Mazuda, Mitsunobu; Fujiwara, Goro, Jpn Kokai Tokk. Koho 10, May 1994.

107. Sugo, Takanobu; Kataoka, Naoaki;Kitagawa, Masami; Tooya, Taisuke; Fujiwara, Kunio; Kawazu, Hideo (Japan Atomic Energy Res. Inst.: Ebara Mfg. Japan) Jpn. Kokai Tokkyo Koho JP 07, 323, 206 [95, 323, 206] (Cl BOID 39/14), 12 Dec. 1995.

108. V.E. Derbisher. T.I. Danilenko, E.V. Darbisher, V.V. Koledov, T.F. Morozenko (Volgogradskii Gosudarstvennyi Tekhni-cheskii Universitet. Russia) Russ. RU 2, 169156 (Cl C08 F8/30), 20 Jun 2001.

109. Sakata, Kunihiro; Nonaka, Masahiro; Jokunaga, Shingo; Suenaga, Joshinori; Hidenori, Shin; Fukiwara, Horo; Hattori, Shinji, Irie, Naoki (NEC Kyushu, Ltd., Jaknma K.K., Japan) Jpn. Kokai Tokkyo Koho JP 09, 157, 990 [97, 157, 990] (Cl D03 D15/00), 17 Jun 1997.

110. Okayama, Yoshika; Matsushima, Mitsuharu; Noguchi, Akihiro; Nawata Hiroyuki; Fujiwara, Goro; Masuda, Mitsunobu; hattori, Shinji; Irie, Naoki (Yamaguchi Nippon Denki K.K.; Takuma K.K, Japan) Jpn. Kokai Tokkyo Koho JP 09 75, 646 [97 75, 646] (Cl. B01 D46/10), 25 Mar. 1997.

111. De Ruiter, Ernest; Toernblom, Jonas (Bluechen G.M.B.H., Germany) Ger. Offen. DE 19, 727, 295 (Cl. B01, D39/14), 7 Jan. 1999.

112. Nagase, Motoki, Fujimura, Yoichi, Asada, Yasuhiro (Toray Industries. Inc., Japan) Jpn. Kokai Tokkyo Koho JP 2002, 282, 625 (Cl B01D39/14), 2 Oct. 2002.

113. Fuiwara, Kuno; Kawazu, Hideo; Katsumata, Kazuki, Akahori, Shoji (Ebara Corp., Japan) Jpn Kokai Tokkyo Koho JP 10179, 708 [78 179. 708] (Cl. A61 L9/16), 7 July 1998.

114. Kato. Naoki.; Shimomura, Makoto (Toshiba Plant Kensetsu Co., Ltd.. Japan) Jpn. Kokai Tokkyo Koho JP 2002, 361, 030 (Cl B01 D53/34). 17 Dec. 2002/173. 161 7 Jun 2001; 6 pp. (Japan).

115. Anon. (Toshiba Plant Kensetsu Co., Ltd., Japan) Sangyo to Kankyo 2002, 31 (4), 42-44 (Japan) Rikku.

116. Lehto, Olavi (Novagent Oy) Finn. FI 95, 876 (Cl. B01J 47/12), 29 Dec. 1995.

117. A.A. Shunkerich, G.I. Sergeev, I.S. Elinson (Inst. Fiz-Org) 1990, 35 (1), 64-72 (Russ.)

118. Uemura, Tadahiro; Kato, Hiroyasu (Toray Ind. Inc. Otsu, Jpn 520) Kurin Tekunoroj 1994, 4(10), 23-7 (Japan).

119. F.W. Petersen. J.W. Coetzee (Dep. Chem. Eng. Cape Technikon, Cape Town, 8000, S. Afr.). Clan Technol. Min. Ind., Proc. Int. Conf. 3'u 1996, 207-217 (Eng.). Edited by Sanchez, A. Mario; Vergara, Froilan; Castro. H. Sergio University of Concepcion: Concepion chile.

120. G.G. Bozhko. V.M. Korukova, O.K. Malysheva (Mosk. Gos. Inst. Stali Splavov, Moscow, Russia).

121. Kotze, H. Martha (Process. Chem. Div.) Mintek, Randburg, S Afr.) JOM 1992, 44(5), 46-50 (Eng.).

122. Rakhmanin, Juri; Maslioukov, Alexandre; Saprikin, Victor; Orlov, Alexandre; Zverev, Mikhail (M-sit France) Eur. Pat.

123. Koide, Fujio; Ochi, Hiroyasu (Nippon Rensui Co., Japan) Jpn. Kokai Tokkyo Koho JP 2003, 24, 714 (Cl B01 D24/00), 28 Jan 2003.

124. Kuwabara, Satoshi; Suehiro, Tetsuko (Nitivy Co., Ltd.) Tokkyo, Japan (104) Kenkyu Hokoku-Sen'i Kabunshi Zairyo Kenkyusho. 1990, (162), 33-6 (Japan).

125. I. Yu. Andreeva, I.L. Min'ko, I. Yu Kazakevich (Leningr. Hos. Univ., Leningrad USSR). Zh. Prikl. Khim (Leningrad), 1991, 64(6), 1276-80 (Russ.).

126. Tang, Hong-Xiao (Research Centre Eco-Environmental Sciences, Chinese Acad. Sci. Beijing, Peop. Rep. China 100085). Fresenius: J. Anal. Chem. (1999) 363 (3), 251-255 (Eng).

127. E. Teremesian, S. Veleva (Bulg). God. Vissh. Khimikotekhnol. Inst., Sofiya 1996 (Pub. 1997). 31 (4), 167-176 (Bulg).

128. Hwang, Tack-Sung; Kim, Young-Su; Park, Jin-Won; Lee, Hyung-Keun (Deptt. of Chemical Engineering, Chungnam National Univ., Daejeon, 305-764 S. Korea) J. of Industrial and Engineering chemistry (Seoul, Republic of Korea) 2004, 10(1), 139-145 (Eng.).

129. R.X. Liu. B.W. Zhang, H.X. Tang (Academia Sinica, Res. Cent. Eco-Environmental Sci., Beijing, Peop. Rep. China 100085) Huanjing Kexue Jinzhan 1996, 4(5), 1-12 (Ch).

130. S.V. Burinskii (St. Petersburg. Gos. Univ. Tekhnol. Dizaina. St. Petersburg, Russia). Khim. Volokna 1996, (6), 16-19 (Russ).

131. Fritz, S. James, Dumont, J. Philips, Hagen. F. Donald, Markele, G. Craig, Schmidt, W. Luther (Minnesota Mining & Mfg. Co.) PCT Int. Appl. W095 30,467 (Cl. B01D15/00), 16 Nov. 1995, US.

132. Henmi, Masahiro; Yoshioka, Toshio (Toray Kobunshi Kenkyusho, Japan). Sen'i Seihin Shohi Kagaku 1990, 31 (10), 454-8 (Japan).

133. Nishi, Takeshi, Matsuda, Masami; Komori Itraru; Babu, Tsutomu; China, Koichi; Ikeda, Takashi; Kikuchi, Jun (Hitachi Ltd.), Jpn, Kokai Tokkyo Koho JP 04,194, 794 [92, 194, 794] (Cl G21 F9/16), 14 Jul 1992.

134. Komatsu, Yu (Natl. Inst. Res. Inorg. Mater. Tsukuba, Japan 305, Nippon Ion Kokon Gakkaishi 1994, 4(3), 202-8 (Japan).

135. Babo, Katsuo (Sumitomo Chemical Co. Ltd) Jpn. Kokai Tokkyo Koho JP 03, 294, 342, [91, 294, 342] (Cl. C08J5/20). 25 Dec., 1991.

136. Tian, Changquing. Wang, Xinquon; Zhang, Dingcai (Zhenghou Textile Institute Zhengzhou Peop. Rep. China 450007) Prog. Saf. Sci. Technology [Proc.. Int. Symp. Saf. Sci. Tech.] 1998, 689-693 (Eng.).

137. Hamamatsu. Takeshi; Asano, Manabu; Sumitani, Tatsuaki; Ibaraki, Akikazu; Mihara, Hirokuni; Tanihata, Kazuki; Kanada, Nobuyasu (Toyobo Co. Ltd., Mitsui Eng and Ship building Co. Ltd., Japan). Jpn. Kokai Tokkyo Koho JP 2000 140, 654, (Cl. B01J47/12), 23 May 2000. Japan.

138. Liu, Ruixia, Wang, Yaxiong, Tang, Hongxiao (State Key Laboratory of Environmental Aquatic Chemistry. Research Center for Eco-Environmental Sciences, Chinese Academy of Science, Beijing, Peop. China 100085). Huanjing Kexue 2002, 23(5), 88-91 (Ch.).

139. Kaneko, Yasuo, Inoe, Nasyuki, Koshimura, Hideo; Matsuno, Hiroshi (Kaneko Shoji K.K.) Jpn. Kokai Tokkyo Koho JP 04, 147, 927 [92, 147, 927] (Cl. C22B19/34) 21 May 1992.

140. K.G. Varsheny, Namrata Tayal, Upma Gupta, Colloids and surf. A: Physiochem. Eng. Aspects, 145 (1998) 71-81.

141. K.G. Varshney, Namrata Tayal, A.A. Khan, R. Niwas, Colloids and Surf. A: Physiochem. Eng. Aspects, 181 (2001) 123-129.

142. K.G. Varshney, Namrata Jayal, Langmuir 17 (2001) 2589-93.

143. G.G. Hawley, The Condensed Chemical Dictionary, Galgotia Booksource, New Delhi; 1984.

144. S.A. Lacks et al., Anal. Biochem. 100, 357 (1979).

145. D.C. Cullum, Introduction of Surfactant Analysis, 1st Ed. Chapman & Hall, U.K., 1994.

146. A.K. De. Environmental Chemistry IInd Ed., Wiley Eastern Limited, Calcutta. 1989.

147. J. Gross, Anionic Surfactants Chemical Analysis, Marcel Dekker, Inc., New York and Basel, 1994.

148. W.M. Linfield Ed. M. Dekker, Anionic Surfactants, New York, 1973.

149. E. Jungermann, Ed., M. Dekker, Cationic Surfactants, New York, (1970).

150. M.V. Nace, Non-ionic Surfactants, Polyoxyethylele Block Copolymers, M. Dekker Inc., New York, Basel & Hong Kong, 1996.

151. M.J. Schick, Ed. M. Dekker, Nonionic Surfactants, New York, 1967.

152. M.R. Porter, Handbook of Surfactants, IInd Ed., U.K. 1994.

153. K.A. Dill, P. Flory, Proc. Natl. Acad. Sci. 78, 676 (1981).

154. C. Tanford, The Hydrophobic Effect, IInd Ed., Wiley, New York, 1980.

155. J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems Academic Press, New York, 1975.

156. P.L. Luisi, B. Straub, Reverse, Micelles- Technological and Biological Relevance, Plenum Press, New York, 1984.

157. M.M. Marquies, H.L. Tiffany, Anal. Biochem. 136, 309 (1984).

158. M.T. Hearn Ed. M. Dekker, Ion-Pair Chromatography, New York, 1985.

159. L.J. Cline, Love et al., Anal. Chem. 56, 1132A (1984).

160. H. Hoffmann, G. Ebert, Angew. Chem. 100, 933 (1988).

Chapter - 2

Synthesis & characterization of n-butyl acetate based Ce(IV) Phosphate, a hybrid fibrous ion exchanger

1. INTRODUCTION

The fibrous ion exchange materials have shown their importance in environmental studies for the separation of harmful ionic impurities due to their high sorption efficiency from gaseous and liquid media.[1-5] The most important property of these fibrous materials is that they can be prepared in various forms, such as cloth, conveyer belts, staples etc, thus opening the door for new technological processes. These fibrous ion exchangers are also used as air filters, water filters and dry scrubbers.

Recently, various hybrid fibrous ion exchangers have been synthesized by combining organic species such as acrylonitrile, acrylamide, styrene, pyridine, pectin etc. with inorganic ion exchangers. The aim to introduce the organic species into an inorganic fibrous material is to enhance reproducibility in behaviour and stability. The materials prepared earlier, such as polyacrylonitrile thorium (IV) phosphate[6], acrylonitrile cerium (IV) phospahate[7], polystyrene Th(IV) phosphate[8] and acrylamide cerium (IV) phosphate[9], have been proved successful in these aspects. They have been used in the separation of various metal ions including heavy metals, thus are of great industrial importance. In this series a new material, n-butyl acetate based Ce(IV) phosphate has been synthesized. Which possesses promising ion exchange characteristics. Following pages summarize the results of such a study.

2. EXPERIMENTAL

2.1 Reagents/chemicals: Ceric sulphate ($Ce(SO_4)_2.4H_2O$] was obtained from CDH (India) while n-butyl acetate ($C_6H_{12}O_2$) and phosphoric acid (H_3PO_4) were obtained from E. Merck (India) and Qualigens (India) respectively. All other reagents and chemicals were of Analar grade.

2.2 Instruments/apparatus used: X-ray diffraction studies were made on a Philips Analytical X-ray B.V. diffractometer type PW 170 B.V. and IR studies were carried out by Shimadzu 8201 spectrophotometer. For TGA/DTA, universal V1.9 DTA instrument was used and SEM studies have been performed by JEOL JSM 840, SM.

2.3 Preparation of reagent solutions: Solutions of ceric sulphate were prepared in 0.5 M H_2SO_4 and those of n-butyl acetate in were prepared in ethanol. A 6 M solution of phosphoric acid was prepared in DMW.

2.4 Synthesis of the ion-exchange materials: A number of samples of n-butyl acetate based Ce (IV) phosphate (nBACP) were prepared by adding one volume of 0.05 M Ce $(SO_4)_2$ solution in 2 volumes of a (1:1) mixture of 6 M H_3PO_4 and n-butyl acetate (0-20%) dropwise with constant stirring using a magnetic stirrer, at a temperature of 60±5°C. The resulting slurry, obtained under these conditions was stirred for 3½ hr. at this temperature, then filtered and washed with DMW till pH~4. Finally, the slurry was dried at room temperature, resulting in a sheet, which was cut into small pieces and converted

into H^+– form by treating with 1 M HNO_3 for 24 hr. with occasional shaking. The material thus obtained, was then washed with demineralised water to remove the excess of acid, and after drying sieved to obtain particles of size 50-70 mesh.

Sn(IV) phosphate was prepared by the methods reported earlier.[10-11]

On the basis of the highest Na^+ ion exchange capacity, sample no (6) was selected for further studies. Table 2.1 shows the ion exchange capacity of various samples of nBACP.

Table 2.1 Synthesis of various samples of n-butyl acetate based Ce (IV) phosphate

Sample No.	% of n-butyl acetate	Na^+–ion exchange capacity (meq/dry g)
nBACP-1	0	1.30
nBACP-2	1	1.45
nBACP-3	3	1.74
nBACP-4	5	1.80
nBACP-5	7	1.90
nBACP-6	8	2.25
nBACP-7	8.5	2.15

nBACP-8	9	2.00
nBACP-9	10	1.60
nBACP-10	12	1.50
nBACP-11	14	1.43
nBACP-12	15	1.25
nBACP-13	20	1.00

2.5 Ion-exchange capacity (i.e.c.): The ion exchange capacity of the sample was determined as usual by the column process taking 1 g of the material (H^+-form) in a glass tube of internal diameter ~ 1 cm, fitted with glass wool at its bottom. 250 mL of 1 M $NaNO_3$ solution was used as eluant, maintaining a very slow flow rate (~0.5 mL min^{-1}). The effluent was titrated against a standard alkali solution to determine the total H^+– ions released Table 2.2 summarizes the ion exchange capacity of the material for various metal ions.

Table 2.2 Ion exchange capacity of nBACP-6 for various metal ions

Metal ion solution (1 M)	Ion-exchange capacity (meq/dry g)
LiCl	2.05
$NaNO_3$	2.25
KCl	2.45
$MgCl_2$	3.00
$Ca(NO_3)_2$	2.59
$SrCl_2$	3.15
$BaCl_2$	2.75

The ion exchange capacity of Sn(IV) phosphate was also determined by the column process and, it was found to be 1.5 meq/dry g.

2.6 Concentration behaviour: To study the effect of eluant concentration on the elution efficiency of the exchanger column, the $NaNO_3$ solution of varying concentrations (0.2 M – 1.2 M) were passed through the column containing 1 g of the exchanger. The effluent was titrated against a standard alkali solution for the H^+ ions eluted out in each case. The optimum concentration of the eluant for a complete elution of H^+ ions in 250 ml of $NaNO_3$ solution was found to be 1 M. Fig. 2.1 shows the variation of the H^+ ions eluted out with the different concentrations of the eluant.

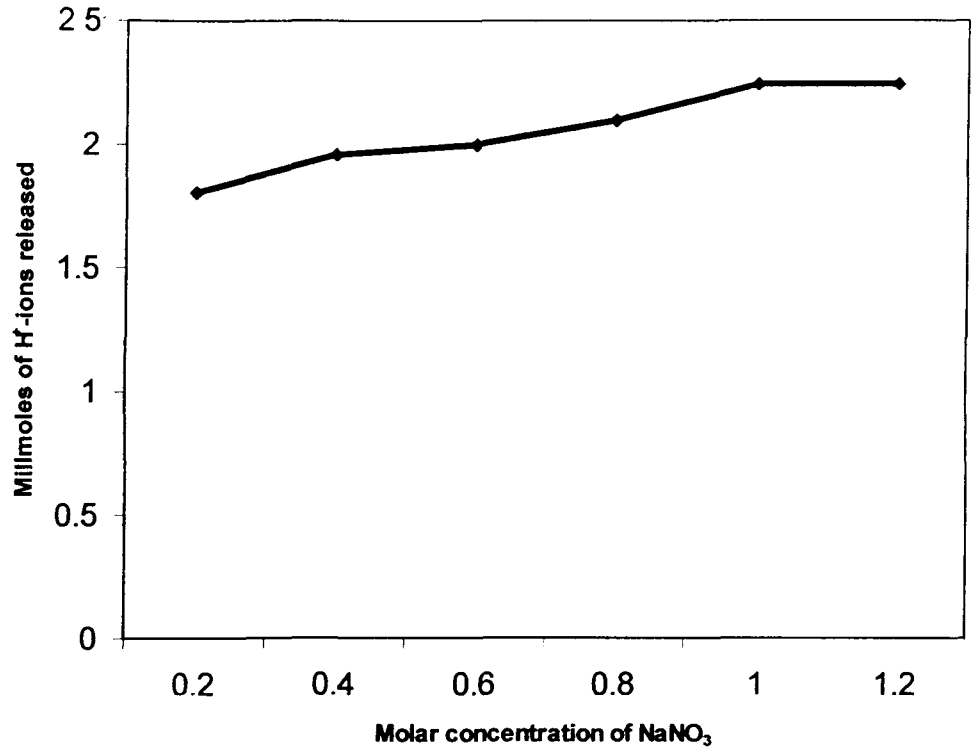


Fig.2.1 Concentration plot of n-butyl acetate based Ce(1V) phosphate

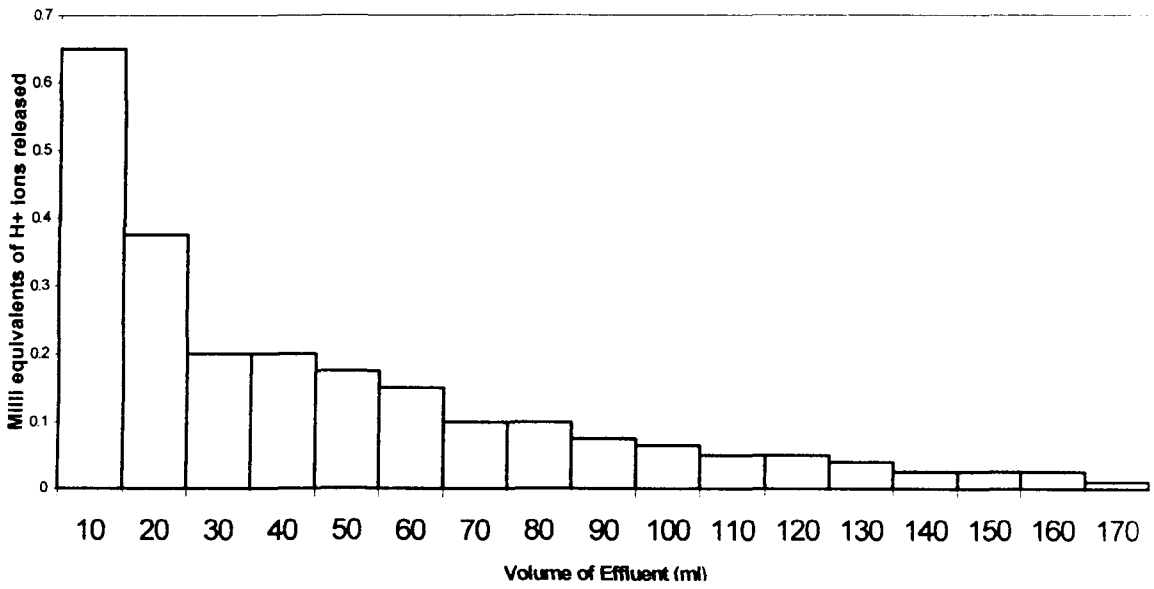


Fig.2.2 Histograms showing the elution behaviour of n-butyl acetate based Ce(IV) phosphate

2.7 Elution Behavour: The column containing 1 g exchanger was eluted with 1 M $NaNO_3$ solution in different 10 mL fractions with a minimum flow rate. This experiment was conducted to find out the minimum volume necessary for a complete elution of H^+ ions, which reflects the efficiency of the column as shown in Fig. 2.2.

2.8 Thermal studies: Different 1 g samples of the material were heated at various temperatures for 1 hr each in a muffle furnace and their ion exchange capacity was determined by the column process after cooling to room temperature. The results are summarized in Table 2.3.

Table 2.3 Thermal stability of n-butyl acetate based Ce(IV) phosphate after heating to various temperatures for 1 hour

Drying temperature (°C)	Na^+-ion exchange capacity (meq/dry g)	Change in colour	% retention of i.e.c.
45	2.25	Yellow	100
100	2.10	Light yellow	93.3
200	1.75	Light yellow	77.8
300	1.50	Creamy yellow	66.7
400	0.85	Creamy yellow	38.0
600	0.31	Off white	14.0
800	0	White	0

2.9 Elemental Analysis: The C&H analysis was carried out by Heraeus Carlo Erba 1108.

2.10 IR studies: The IR spectrum was taken by KBr disc method and is given in Fig. 2.3.

2.11 X-ray studies: Fig. 2.4 shows the X-ray diffraction pattern of the material.

2.12 Scanning electron micrograph studies: Fig. 2.5 shows the electron micrograph of the material.

2.13 Thermogravmetric analysis and differential thermal analysis: Fig. 2.6 shows the TGA/DTA curves of the material.

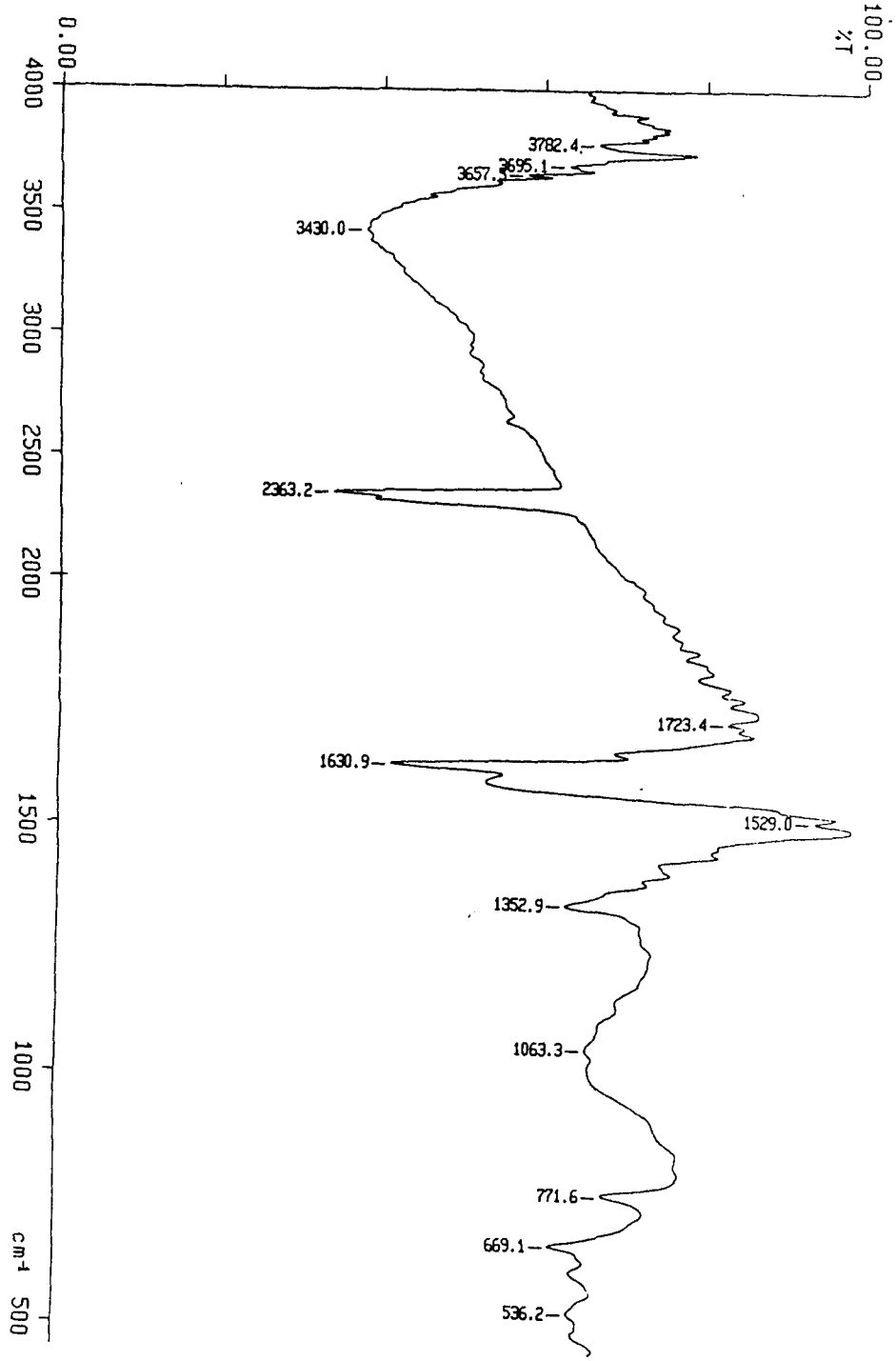


Fig. 2.3 IR Spectrum of n-butyl acetate based Ce(IV) phosphate

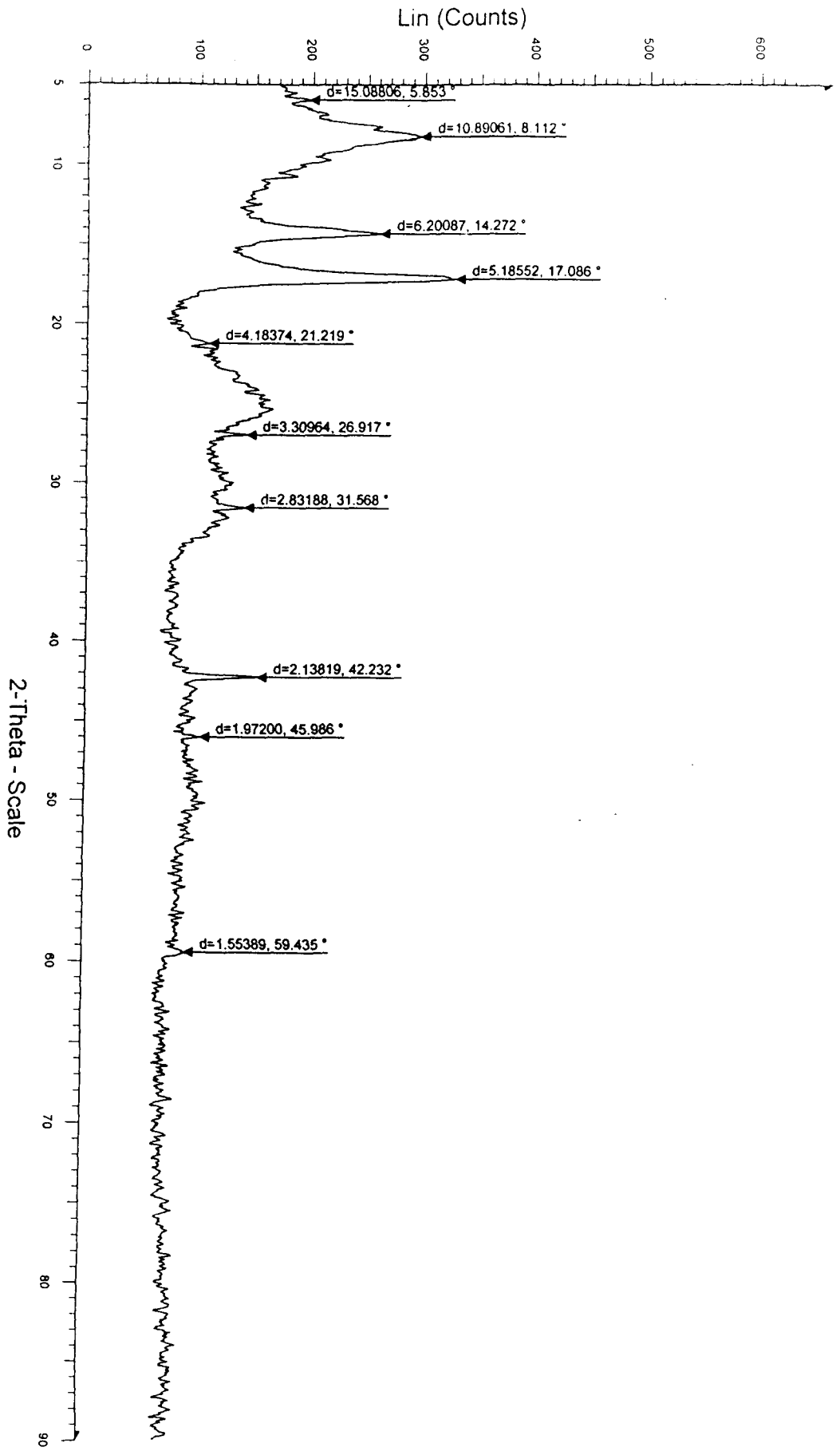


Fig. 2.4 X-ray diffraction pattern of n-butyl acetate based Ce(IV) phosphate

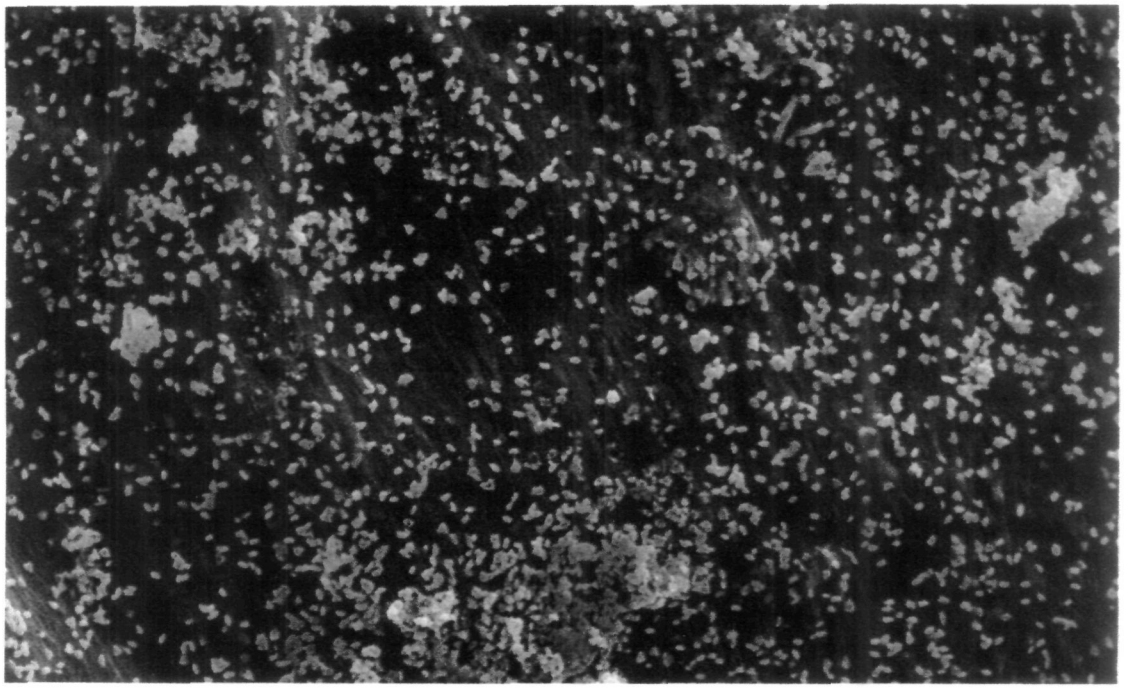


Fig. 2.5 Scanning electron micrograph of nBACP

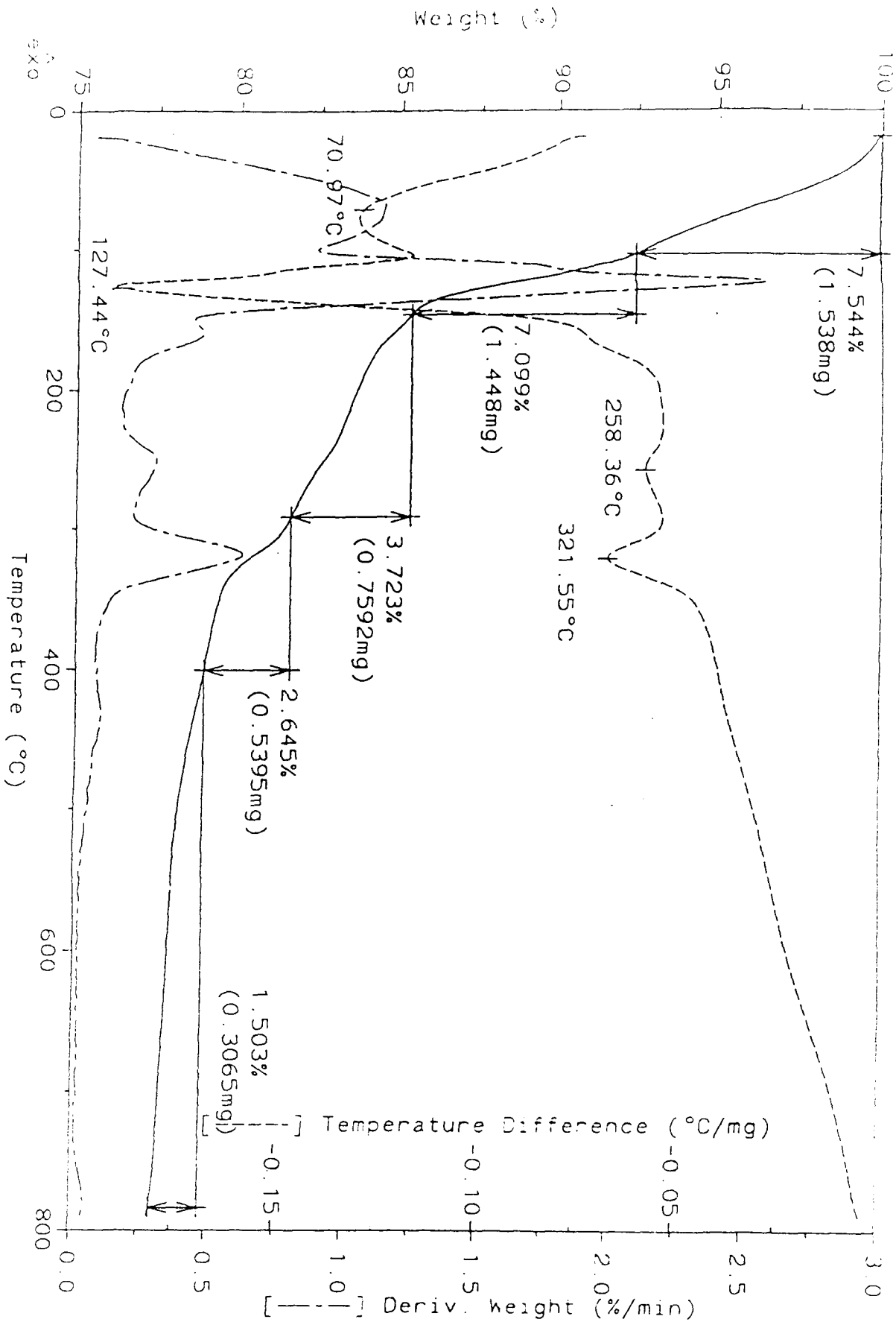


Fig. 2.6 TGA-DTA curves of n-butyl acetate based Ce(IV) phosphate

3. RESULTS AND DISCUSSION

n-butyl acetate based Cerium (IV) phosphate (nBACP), a new hybrid fibrous ion exchanger has been synthesized, possessing a good Na^+-ion exchange capacity (2.25 meq/dry g) which is higher than the ion exchange capacity of inorganic ion exchangers, prepared earier.[12-14] Further, the material is obtained in the sheet form which is clear from the SEM studies of the material showing the fibrous nature of the material.

The thermal stability of the material appears to be less than the normal inorganic ion exchangers, which may be due to the presence of the organic part in its structure. It retains 38% of its ion exchange capacity on heating upto 400°C. However, on comparing with other fibrous ion exchangers, prepared earlier such as acrylonitrile Ce (IV) phosphate, polyacrylonitrile Th (IV) phosphate and acrylamide Ce (IV) phosphate n-butyl acetate based Ce (IV) phosphate is found thermally more stable.

The concentration behaviour (Fig. 2.1) indicates that 250 mL of a 1M solution of the eluant ($NaNO_3$) can completely elute the H^+ ions from a 1 g exchanger column. Further, the elution behaviour shows that the exchange is quite fast and almost all the H^+ ions are eluted out in the first 190 mL of the effluent from a column of 1 g exchanger (Fig. 2.2).

The TGA/DTA curves (Fig. 2.6) show the 7.5% loss of weight upto 127°C, which may be due to the removal of external water molecules. Beyond

127°C. the condensation of the material must have started, resulting in the dehydration due to the removal of the strongly coordinated water molecules from the framework of exchangers, which continues upto 400°C where the weight becomes almost constant. It also involves the production of CeO_2 at 450°C.[15]

On the basis of its elemental analysis, the material contains 0.49% carbon and 1.62% hydrogen.

The IR studies[16] confirm the presence of metal oxygen and metal hydroxide bonds in addition to the external water molecules in the material. The metal-oxygen and metal-hydroxide bands are observed at 669.1 cm^{-1} while bands at 1630.9 cm^{-1} and 3430 cm^{-1} are due to the external water molecules. The bands beyond 3430cm^{-1} are due to the free –OH groups of the external water molecules (or, the alcohol formed by the n-butyl acetate). The bands at 536.2 cm^{-1} and 1063.3 cm^{-1} indicate the presence of phosphate groups. While the bands[17] at 1723.4 and 1529 cm^{-1} represent the C=O and C–O stretchings. The C–C stretching and COO^- group are represented by the bands at 771.6 and 1352.9 cm^{-1} respectively.

The X-ray diffraction pattern of the material exhibits weak peaks indicating its poorly crystalline or amorphous nature.

References

1. M.P. Zverew, Chemisorptive fibres, Khimiya, Moscow, 1981.

2. L.A. Wolf, Fibres of Specific Properties, Khimiya, Moscow, 1980.

3. I.N. Ermolenbo, E.D. Bugalov, I.P. Lyublinder, S.R. Nanka'I Tebhniba, Minsk, 1975.

4. L.A. Wolf, Chem. – Ind. (Bulgaria) 3 (1983) 53.

5. T. Miyamatsu, Sen'I Gabbaishi 39 (1983) 53.

6. K.G. Varshney, Namrta Tayal, A.a. Khan and R. Niwas, Colloids Surf. A: Physiochem. Eng. Asp. 181 (2001) 123.

7. K.G. Varshney, Namrta & U. Gupta, Colloids A: Physiochem. Eng. Asp., 145 (1998) 71.

8. K.G. Varshney & Namrta Tayal, Langmuir, 17 (2001) 2589.

9. K.G. Varshney, Puja Gupta & Namrta Tayal, Ind. J. Chem. 42A (2003) 89.

10. U.Costantino and A. Gasperoni, J. Chromatogr., 51, 289 (1970).

11. M.J. Fuller, J. Inorg. Nucl. Chem., 33, 559 (1971).

12. K.G. Varshney, A.A. Khan, R. Niwas, P.K. Parashan & K.T. Nasim, Ind. J. Chem. Technol. 4 (1997) 317.

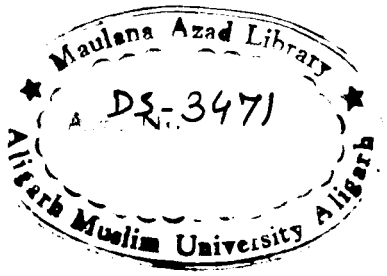
13. K.G. Varshney, Alka Gupta, K.G. Singhal, Colloids Surf. A: Physiochem. Eng. Asp., 82 (1994) 37.

14. K.G. Varshney, Alka Gupta & K.G. Singhal, Ind. J. Chem., 34A (1995) 888.

15. C. Duval, Inorganic Thermogravimetric analysis Elsevier, Amsterdam, (1963) p. 130.

16. C.N.R. Rao, Chemical applications of infrared spectroscopy Academic Press, New York (1963).

17. P.S. Kalsi, Spectroscopy of organic compounds, 5th Ed. (2002).



Chapter - 3

Adsorption behaviour of n-butyl acetate based Ce(IV) phosphate & Sn(IV) phosphate for some alkaline earths & heavy metal ions: Effect of surfactants

1. INTRODUCTION

Inorganic ion exchangers have been of great interest in the selective adsorption and removal of metal ions from aqueous systems. A large number of such materials have been studied during the last few decades. They are generally the polybasic acid salts of multivalent metals, such as Ce(IV), Th(IV), Zr(IV), Ti(IV) and Sn(IV), phosphates, tungstates, arsenates, and silicates. Some of these materials have shown fibrous behaviour which has opened a new area of research by forming their different textile goods. Ce(IV) phosphate has been found earlier[1-4] to be a quite successful as fibrous ion exchanger while Sn(IV) phosphate[5-6] has been found useful as a non-fibrous ion exchanger.

Surfactants are the substances which are surface active and can play a lead role in modifying the adsorption behaviour of the ion exchange materials. They have been studied for such applications and found effectively useful. The present study is undertaken to explore the potential of surfactants in modifying the adsorption properties of inorganic fibrous and non-fibrous ion exchange materials. Following pages summarize the results of such a study on both types of the ion exchangers namely fibrous and non-fibrous. Ce (IV) phosphate and Sn(IV) phosphate have been selected as the representative materials of these two categories respectively.

2 EXPERIMENTAL

2.1 Surfactants used: Triton X-100 ($C_{34}H_{62}O_{11}$) and dodecyl benzne sulphonic acid sodium salt ($C_{18}H_{29}SO_3Na$) were obtained from Himedia (India) while N-cetyl-N,N,N-trimethyl ammonium bromide ($C_{19}H_{42}NBr$), sodium dodecyl sulphate ($C_{12}H_{25}SO_4Na$) and N-dodecyl pyridinium chloride ($C_{17}H_{30}ClN$) were obtained from CDH (India), BDH (India) and Merck-schuchardt (Germany) respectively.

2.2 Preparation of the surfactant solutions: Solutions of the surfactants were prepared in demineralised water taking concentrations of all, below CMC, at CMC and above CMC values. Table 3.1 shows the chemical formulae and CMC values of the surfactants, used.

Table 3.1 Chemical formulae and CMC values of the used surfactants

Surfactants	Chemical formula/structure	CMC values (m/lit)
Anionic		
Sodium dodecyl sulphate (SDS)	$[CH_3(CH_2)_{11}OSO^-{}_3Na^+]$	8.1×10^{-3}
Sodium dodecyl benzene sulphonate (SDBS)	$[CH_3(CH_2)_{11}C_6H_4SO^-{}_3Na^+]$	1.2×10^{-3}
Cationic		
N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB)	$[CH_3(CH_2)_{15}](CH_3)_3N^+Br^-$	9×10^{-4}
N-dodecyl pyridinium chloride (DPC)	$[CH_3(CH_2)_{11}]N^+C_5H_5\ Cl^-$	1.5×10^{-2}
Nonionic		
Triton X-100 (TX-100)	$(CH_3)_2CH(CH_2)_5\text{-}C_6H_4O(CH_2CH_2O)_{10}H$	2.8×10^{-4}

2.3 Adsorption Studies

200 mg of the exchangers (nBACP and SnP) in the H^+-form were added to a mixture containing 18 mL of the acid solution and 2 mL of the metal ion solution. The mixture was kept for 24 hours, shaking intermittently, to achieve equilibrium. The metal ions in the solution before and after equilibrium were determined by the EDTA titrations and the distribution coefficients (Kd) were calculated by the formula:

$$Kd = \frac{I-F}{F}\frac{V}{M}(mLg^{-1})$$

where I and F are the initial and final amounts of the metal ions in the solution phase, V the volume (mL) of the solution, and M the amount (g) of the exchanger.

The above experiment was repeated by taking surfactant solution instead of the acid solution in the same amount (18 mL).

The distribution coefficients (Kd) obtained for the metal ions studies in different media are summarized in Table 3.2 to 3.13. Figures 3.1 to 3.16 show the concentration dependence of Kd-values in these media for both nBACP & SnP ion exchangers.

Table 3.2 Kd-values of metal ions on nBACP in DMW, hydrochloric acid, nitric acid and perchloric acid media.

Metal ions	DMW	HCl			HNO_3			$HClO_4$		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	2200.0	2200.0	1433.3	666.67	820.00	475.80	411.11	820.00	475.00	318.18
Ca(II)	820.00	475.00	411.11	360.00	360.00	360.00	253.85	666.67	360.00	206.67
Sr(II)	800.00	309.09	275.00	200.00	400.00	309.09	114.29	800.00	246.15	200.00
Ba(II)	616.67	437.50	330.00	290.91	377.78	377.78	330.00	514.29	514.29	290.91
Mn(II)	666.67	820.00	475.00	130.00	557.14	253.85	187.50	206.67	170.59	130.00
Fe(III)	740.00	5000.00	320.00	90.900	500.00	500.00	425.00	950.00	950.00	600.00
Co(II)	950.00	1300.0	740.00	500.00	32.00	281.82	223.08	180.00	162.50	68.000
Ni(II)	254.55	TA	284.62	150.00	233.33	212.50	138.09	150.00	138.10	108.30
Cu(II)	1566.7	900.00	614.29	614.29	900.00	733.33	614.29	733.33	614.29	614.29
Cd(II)	1075.0	840.00	840.00	571.43	1075.0	1075.0	840.00	84.00	571.43	370.00
Hg(II)	4400.0	2150.0	1400.0	1025.0	1025.0	10.25.0	800.00	4400.0	2150.0	1400.0
Pb(II)	542.86	462.50	309.09	200.00	462.50	200.00	50.000	350.00	350.00	95.650

Table 3.3 Kd-values of metal ions on nBACP in sodium dodecyl sulphate (SDS) solutions

Metal ions	SDS				
	0.001M	**0.005 M**	**0.01M**	**0.05M**	**0.1M**
Mg(II)	557.14	557.14	557.14	557.14	557.14
Ca(II)	557.14	557.14	557.14	557.14	557.14
Sr(II)	800.00	800.00	800.00	800.00	800.00
Ba(II)	975.00	975.00	975.00	975.00	975.00
Mn(II)	1050.0	1050.0	1433.3	557.14	360.00
Fe(III)	110.00	180.00	366.67	68.000	0
Co(II)	500.00	950.00	1300.0	950.00	740.00
Ni(II)	150.00	177.78	233.33	163.16	117.39
Cu(II)	400.00	400.00	455.56	354.54	284.62
Cd(II)	683.33	1075.0	1466.7	1075.0	1075.0
Hg(II)	1400.0	800.00	350.00	1025.0	650.00
Pb(II)	1400.0	1400.0	2150.0	1400.0	1400.0

Table 3.4 Kd-values of metal ions on nBACP in sodium dodecyl benzene sulphonate (SDBS) solutions

Metal ions	SDBS				
	0.0001M	**0.0005 M**	**0.001M**	**0.005M**	**0.01M**
Mg(II)	557.14	557.14	557.14	557.14	557.14
Ca(II)	820.00	820.00	820.00	820.00	820.00
Sr(II)	800.00	800.00	800.00	800.00	800.00
Ba(II)	760.00	760.00	760.00	760.00	760.00
Mn(II)	1433.3	1433.3	1433.3	1433.3	1433.3
Fe(III)	223.08	320.00	366.67	180.00	44.830
Co(II)	740.00	950.00	1300.0	740.00	500.00
Ni(II)	66.670	177.78	400.00	316.67	233.33
Cu(II)	733.33	733.33	900.00	400.00	316.67
Cd(II)	1075.0	1466.6	2250.0	1466.6	1466.6
Hg(II)	2150.0	2150.0	2150.0	800.00	275.00
Pb(II)	800.00	1025.0	2150.0	1400.0	1400.0

Table 3.5 Kd-values of metal ions on nBACP in cetyl trimethyl ammonium bromide (CTAB) solutions

Metal ions	CTAB			
	0.0005M	**0.001 M**	**0.005M**	**0.01M**
Mg(II)	820.00	557.14	820.00	1050.00
Ca(II)	1050.0	666.67	820.00	1050.0
Sr(II)	650.00	542.86	650.00	800.00
Ba(II)	760.00	616.67	975.00	975.00
Mn(II)	666.67	475.00	820.00	820.00
Fe(III)	320.00	23.530	121.050	180.00
Co(II)	425.00	366.67	425.00	425.00
Ni(II)	525.00	354.54	400.00	455.56
Cu(II)	1150.0	614.28	900.00	1150.0
Cd(II)	1075.0	571.42	683.33	840.00
Hg(II)	1400.0	800.00	1025.0	1025.0
Pb(II)	2150.0	1400.0	1400.0	1400.0

Table 3.6 Kd-values of metal ions on nBACP in 1-dodecyl pyridinium chloride (DPC) solutions

Metal ions	DPC				
	0.001M	**0.005 M**	**0.01M**	**0.05M**	**0.1M**
Mg(II)	666.67	557.14	475	557.14	557.14
Ca(II)	820.00	666.67	557.14	666.67	666.67
Sr(II)	800.00	800.00	650.00	1025.0	1025.0
Ba(II)	514.29	437.50	377.78	377.78	437.50
Mn(II)	557.14	557.14	411.10	475.00	475.00
Fe(III)	250.00	180.00	20.000	133.33	133.33
Co(II)	320.00	320.00	281.81	320.00	320.00
Ni(II)	614.29	525.00	455.56	525.00	525.00
Cu(II)	733.33	733.33	614.29	733.33	733.33
Cd(II)	1075.0	840.00	683.33	840.00	840.00
Hg(II)	2150.0	1400.0	1025.0	1400.0	1400.0
Pb(II)	2150.0	1400.0	800.00	1025.0	1025.0

Table 3.7 Kd-values of metal ions on nBACP in Triton X-100 (TX-100) solutions

Metal ions	TX-100				
	0.00001M	**0.00005 M**	**0.0001M**	**0.0005M**	**0.001M**
Mg(II)	1050.0	1050.0	1050.0	1050.0	TA
Ca(II)	1433.33	1433.33	1433.33	2200.0	TA
Sr(II)	1025.0	1025.0	1025.0	2150.0	TA
Ba(II)	760.00	975.00	975.00	1333.33	4200.0
Mn(II)	1433.3	1433.3	1433.3	1433.3	1433.3
Fe(III)	2000.0	2000.0	2000.0	TA	TA
Co(II)	950.00	950.00	950.00	1300.0	2000.0
Ni(II)	900.00	900.00	1150.0	2400.0	2400.0
Cu(II)	1566.6	1566.6	1566.6	2400.0	4900.0
Cd(II)	683.33	683.33	1075.0	1466.6	1466.6
Hg(II)	4400.0	4400.0	4400.0	4400.0	TA
Pb(II)	2150.0	2150.0	2150.0	TA	TA

Table 3.8 Kd-values of metal ions on SnP in DMW, hydrochloric acid, nitric acid and perchloric acid

Metal ions	DMW	HCl			HNO_3			$HClO_4$		
		0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M	0.01 M	0.1 M	1 M
Mg(II)	16.25	162.5	147.0	133.3	320.0	281.8	200.0	366.6	320.0	200.0
Ca(II)	192.9	215.4	173.3	156.2	192.9	173.3	127.8	272.7	215.4	141.2
Sr(II)	330	377.8	258.3	230.8	616.7	616.7	377.8	330.0	290.9	168.7
Ba(II)	90.00	700.0	700.0	471.4	566.7	400.0	207.7	471.4	344.4	207.7
Mn(II)	104.4	88.00	80.80	56.70	95.80	88.00	74.10	422.2	327.3	235.7
Fe(III)	160.0	143.7	129.4	105.0	160.0	143.7	105.3	225.0	178.6	105.3
Co(II)	330.0	377.8	258.3	186.7	514.3	330.0	230.8	437.5	377.8	186.7
Ni(II)	41.40	36.70	32.30	28.10	36.70	24.20	17.10	95.20	78.30	64.00
Cu(II)	666.7	557.1	360.0	206.7	411.1	360.0	253.8	557.1	360.0	253.8
Cd(II)	311.1	270.0	184.6	146.7	164.3	146.7	105.6	184.6	160.0	131.2
Hg(II)	500.0	500.0	320.0	223.1	500.0	425.0	281.8	740.0	500.0	425.0
Pb(II)	164.7	164.7	150.0	114.3	462.5	400.0	246.2	650.0	542.9	309.1

Table 3.9 Kd-values of metal ions on SnP in sodium dodecyl sulphate (SDS) solutions

Metal ions	SDS				
	0.001M	0.005 M	0.01M	0.05M	0.1M
Mg(II)	320.0	320.0	320.0	320.0	320.0
Ca(II)	310.0	310.0	310.0	310.0	310.0
Sr(II)	760.0	760.0	760.0	760.0	760.0
Ba(II)	900.0	900.0	900.0	900.0	900.0
Mn(II)	840.0	683.3	487.5	571.4	1075
Fe(III)	457.1	387.5	333.3	457.1	457.1
Co(II)	2050	2050	1333	2050	4200
Ni(II)	355.6	355.6	310	355.6	412.5
Cu(II)	820.0	820.0	666.7	820.0	1050
Cd(II)	640.0	428.6	270.0	362.5	428.6
Hg(II)	950.0	2000	2000	2000	2000
Pb(II)	800.0	650.0	462.5	542.9	650.0

Table 3.10 Kd-values of metal ions on SnP in sodium dodecyl benzene sulphonate (SDBS) solutions

Metal ions	SDBS				
	0.0001M	**0.0005 M**	**0.001M**	**0.005M**	**0.01M**
Mg(II)	366.7	366.7	366.7	366.7	366.7
Ca(II)	412.5	412.5	412.5	412.5	412.5
Sr(II)	616.7	616.7	616.7	616.7	616.7
Ba(II)	700.0	700.0	700.0	700.0	700.0
Mn(II)	571.4	422.2	327.3	487.5	487.5
Fe(III)	550.0	457.1	333.3	457.1	457.1
Co(II)	1333	975.0	760.0	975.0	975.0
Ni(II)	925.0	720.0	583.3	720.0	720.0
Cu(II)	820.0	666.7	475.0	666.7	666.7
Cd(II)	825.0	428.6	362.5	428.6	428.6
Hg(II)	950.0	740.0	600.0	740.0	740.0
Pb(II)	1400	800.0	542.9	650.0	800.0

Table 3.11 Kd-values of metal ions on SnP in cetyl trimethyl ammonibromide (CTAB) solutions

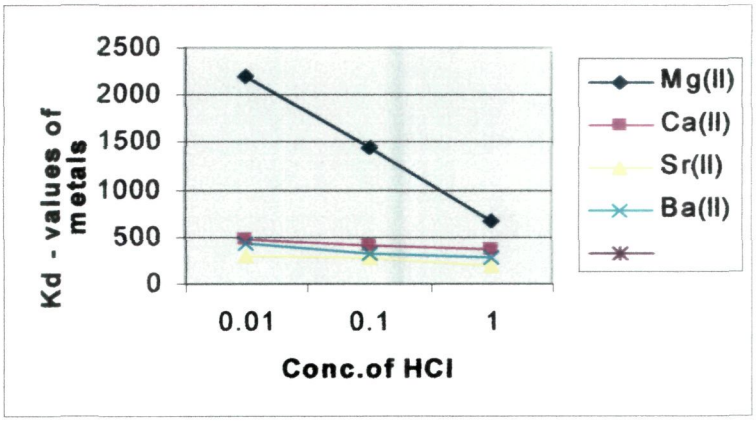
Metal ions	CTAB			
	0.0005M	**0.001 M**	**0.005M**	**0.01M**
Mg(II)	500.0	600.0	600.0	600.0
Ca(II)	720.0	925.0	925.0	925.0
Sr(II)	760.0	760.0	975.0	975.0
Ba(II)	700.0	900.0	900.0	900.0
Mn(II)	571.4	683.3	840.0	840.0
Fe(III)	333.3	387.5	457.1	457.1
Co(II)	514.3	616.7	760.0	760.0
Ni(II)	310.0	485.7	583.3	583.3
Cu(II)	557.1	666.7	820.0	820.0
Cd(II)	362.5	428.6	825.0	825.0
Hg(II)	740.0	1300	2000	2000
Pb(II)	542.9	1025	1400	1400

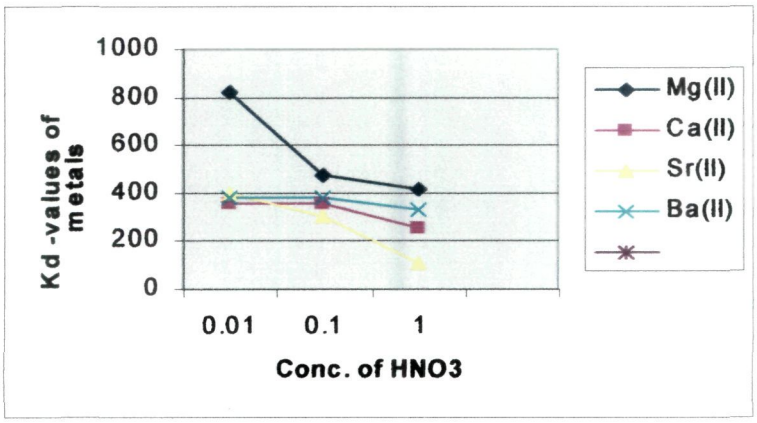
Table 3.12 Kd-values of metal ions on SnP in 1-dodecyl pyridinium chloride (DPC) solutions

Metal ions	DPC				
	0.001M	**0.005 M**	**0.01M**	**0.05M**	**0.1M**
Mg(II)	500.0	740.0	950.0	950.0	950.0
Ca(II)	583.3	720.0	720.0	720.0	720.0
Sr(II)	760.0	975.0	975.0	975.0	975.0
Ba(II)	700.0	900.0	900.0	900.0	900.0
Mn(II)	422.2	487.5	571.4	683.3	683.3
Fe(III)	387.5	457.1	457.1	550.0	550.0
Co(II)	514.3	616.7	760.0	975.0	975.0
Ni(II)	173.3	241.7	310.0	412.5	412.5
Cu(II)	557.1	666.7	820.0	1050	1050
Cd(II)	516.7	640.0	640.0	825.0	825.0
Hg(II)	740.0	950.0	2000	4100	TA
Pb(II)	542.9	800.0	1025	1400	1400

Table 3.13 Kd-values of metal ions on SnP in Triton X-100 (TX-100) solutions

Metal ions	TX-100				
	0.00001M	**0.00005 M**	**0.0001M**	**0.0005M**	**0.001M**
Mg(II)	366.7	500.0	600.0	950.0	1300
Ca(II)	310.0	583.3	720.0	925.0	1950
Sr(II)	290.9	377.8	616.7	760.0	975.0
Ba(II)	263.6	400.0	700.0	900.0	1233
Mn(II)	422.2	571.4	1075	1466	2250
Fe(III)	550.0	680.0	875.0	3800	TA
Co(II)	514.3	760.0	1333	4200	TA
Ni(II)	215.4	272.7	412.5	583.3	1950
Cu(II)	820.0	1050	1433	4500	TA
Cd(II)	428.6	680.0	825.0	1750	TA
Hg(II)	740.0	950.0	4100	TA	TA
Pb(II)	800.0	1400	2150	TA	TA





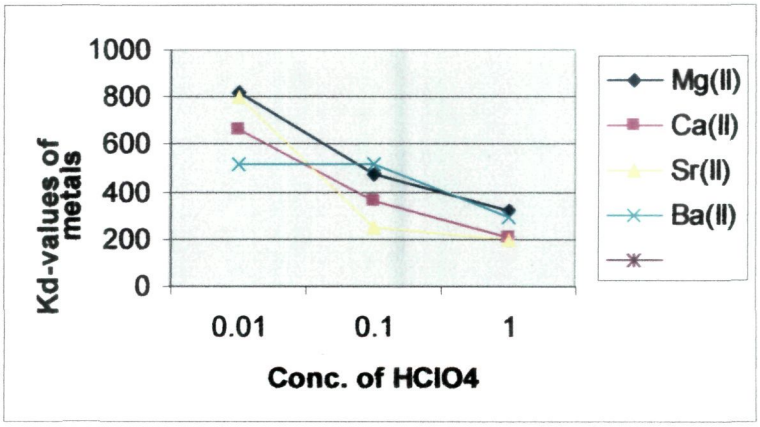
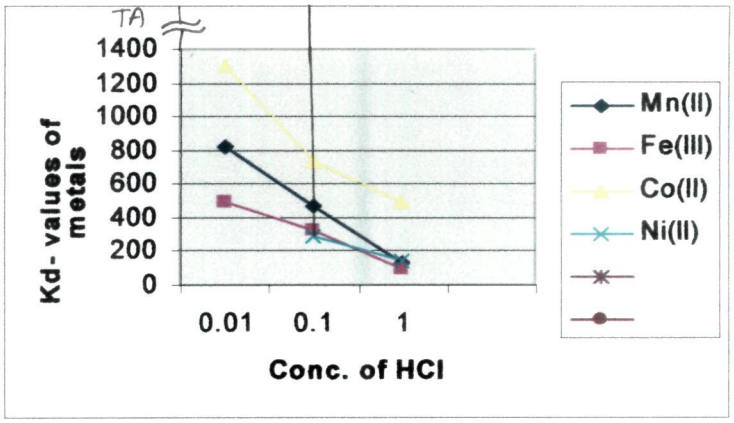
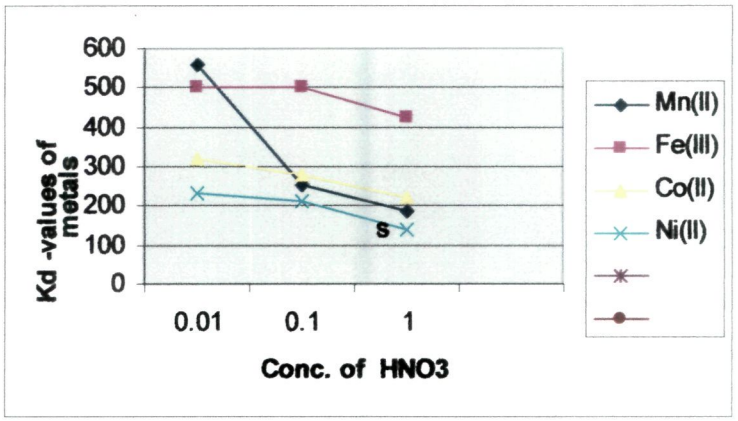


Fig.3.1 Kd-values vs. acid concentrations plots for alkaline earths on nBACP.





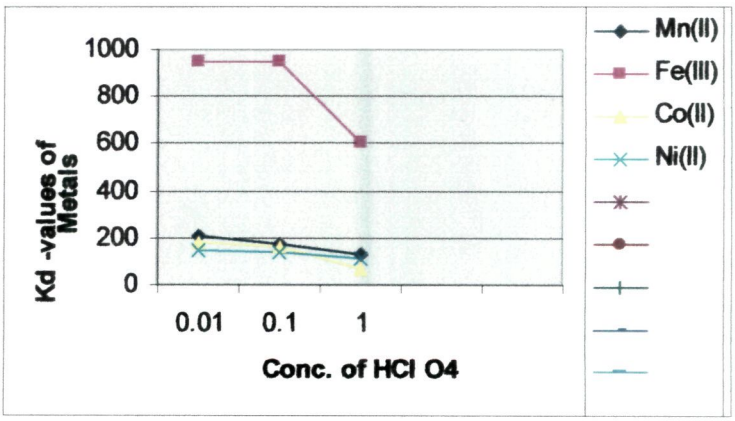
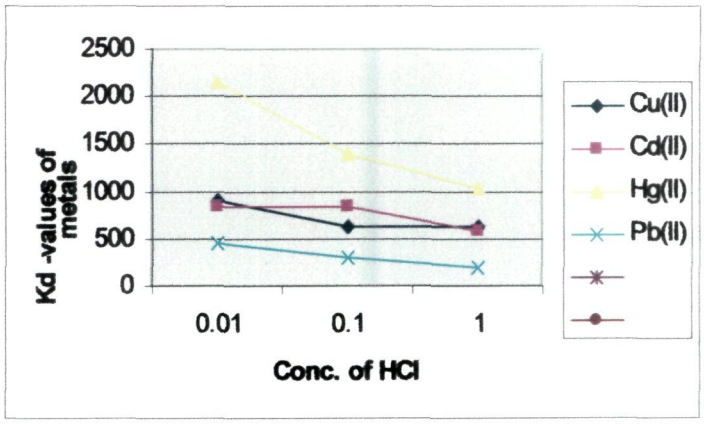
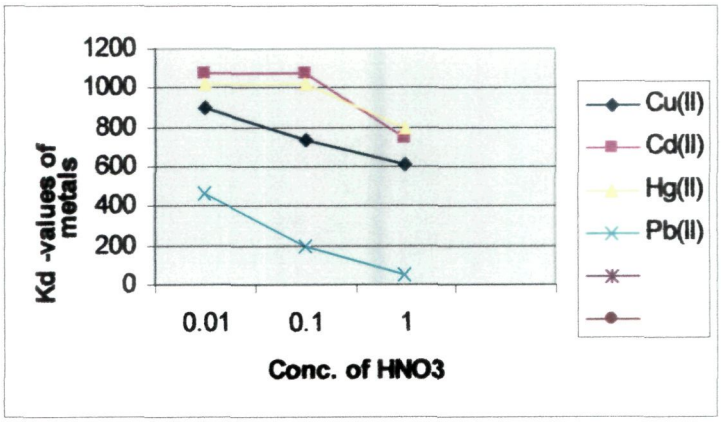


Fig.3.2 Kd-values vs. acid concentrations plots for heavy metals on nBACP.





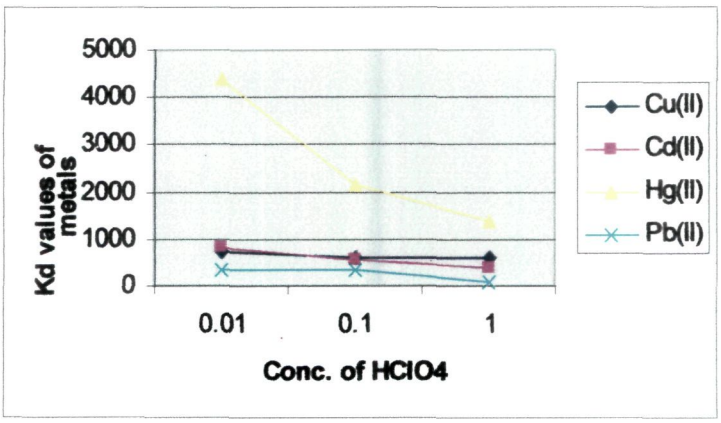


Fig.3.3 Kd-values vs. acid concentrations plots for heavy metals on nBACP.

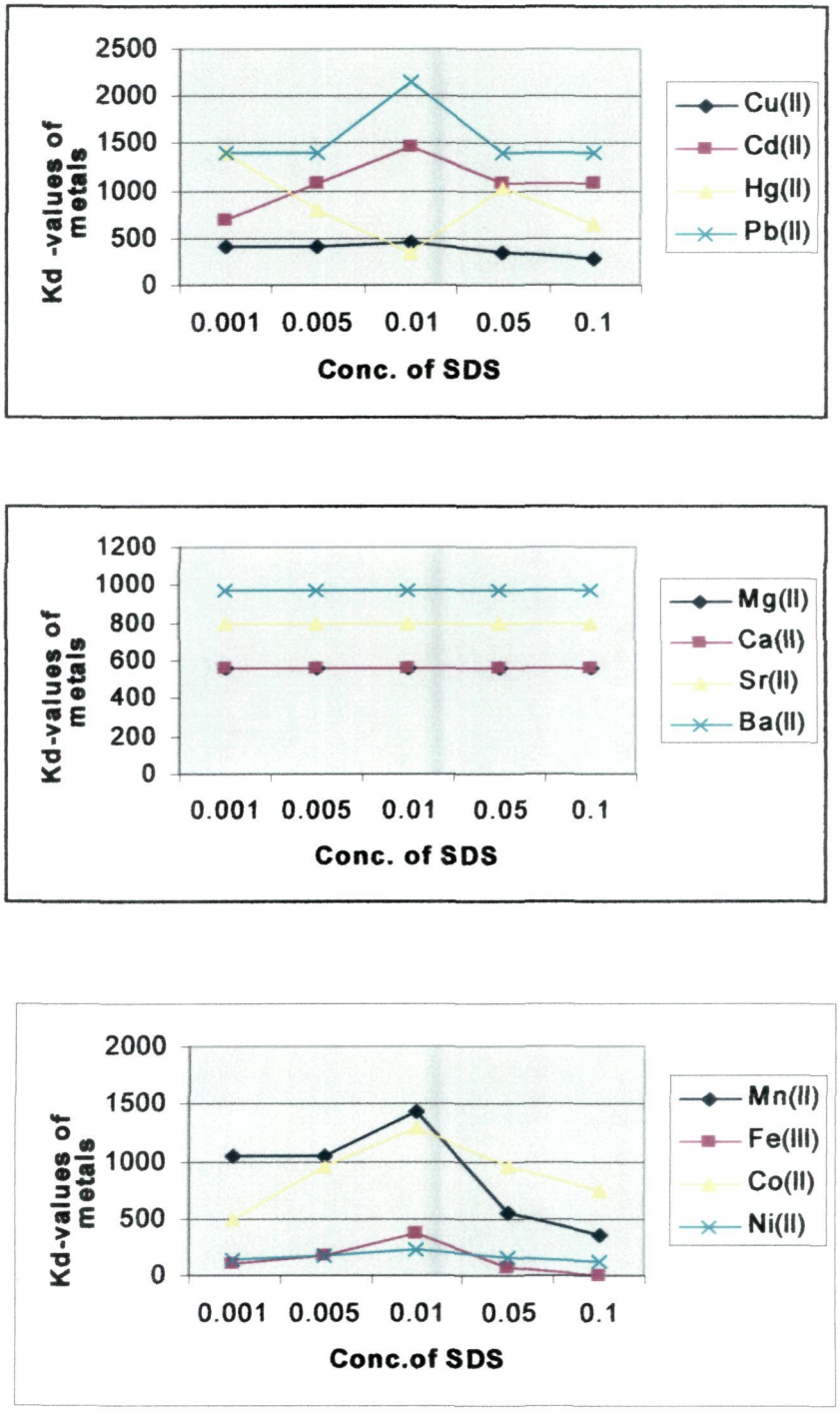
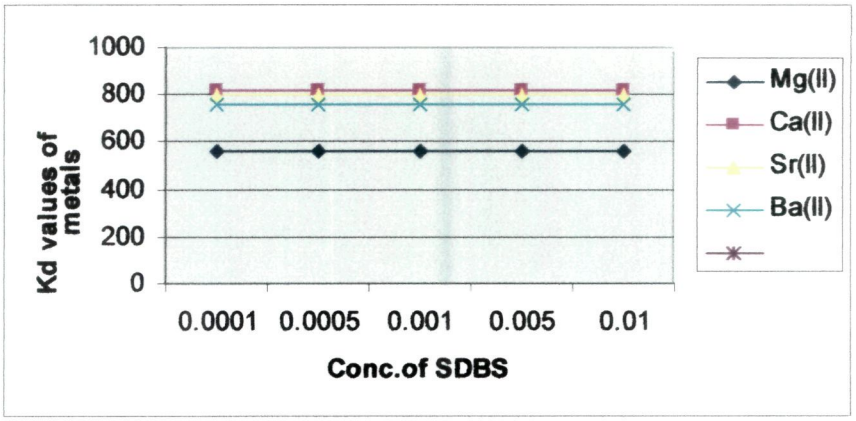
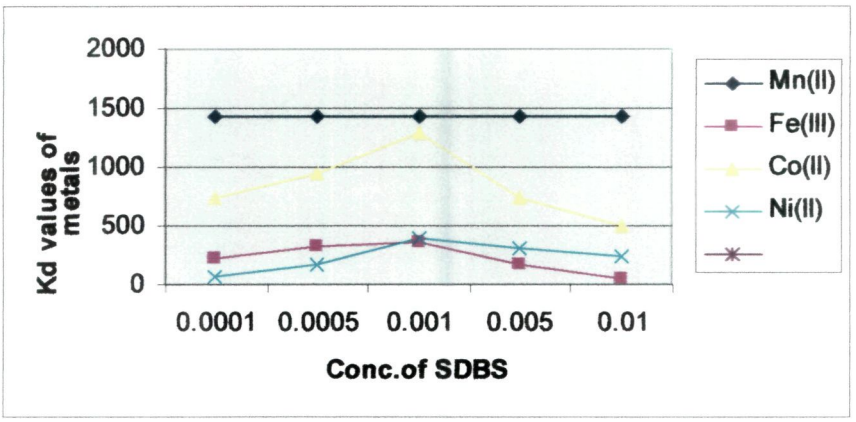


Fig. 3.4 Kd-values vs. SDS concentrations plots for alkaline earths & heavy metals on nBACP.





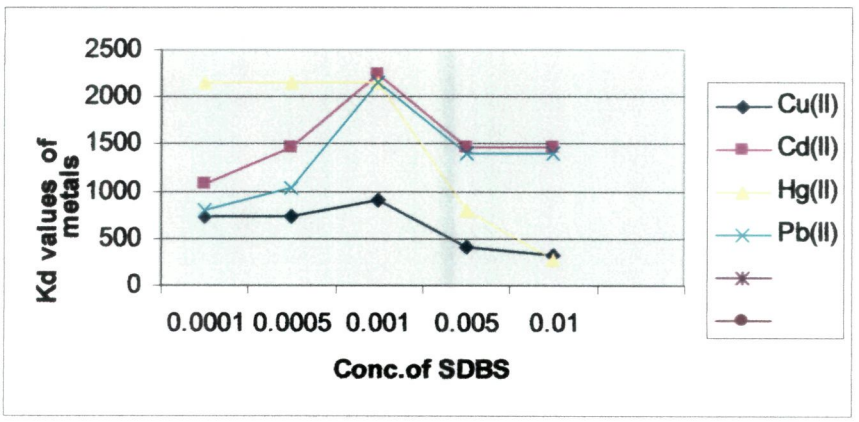
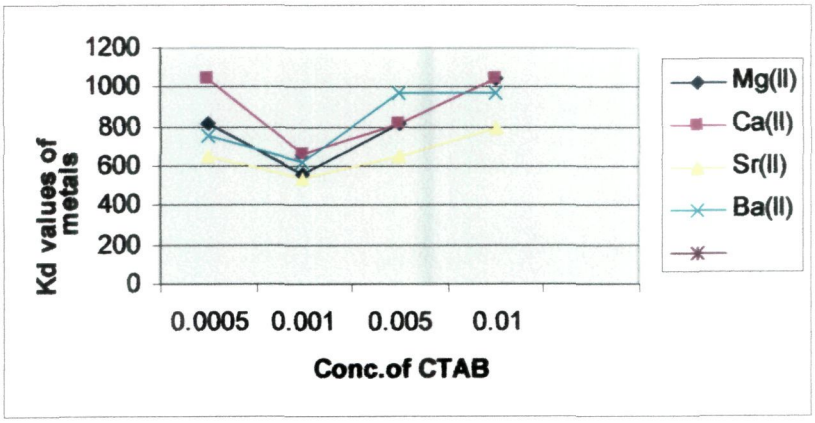
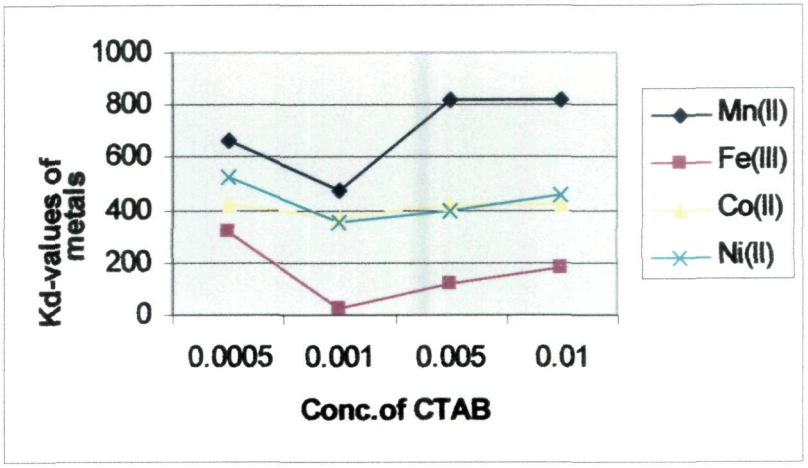


Fig. 3.5 Kd-values vs. SDBS concentrations plots for alkaline earths & heavy metals on nBACP.





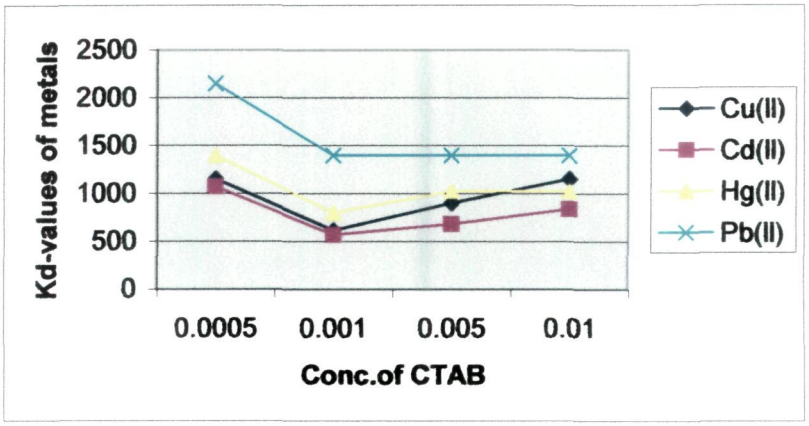
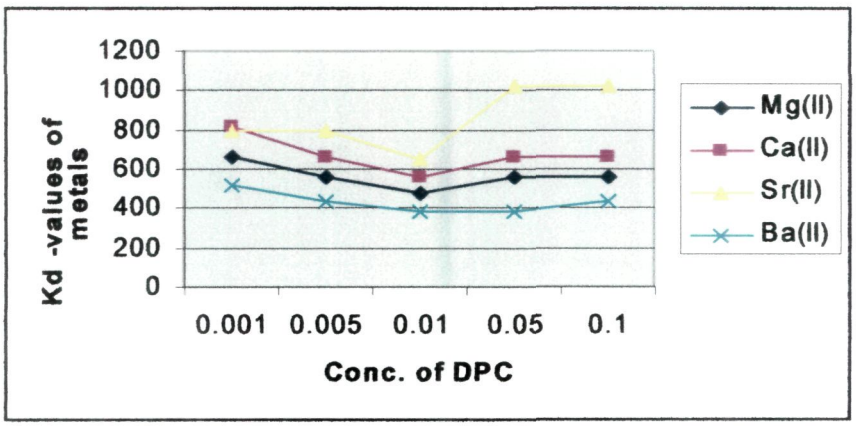
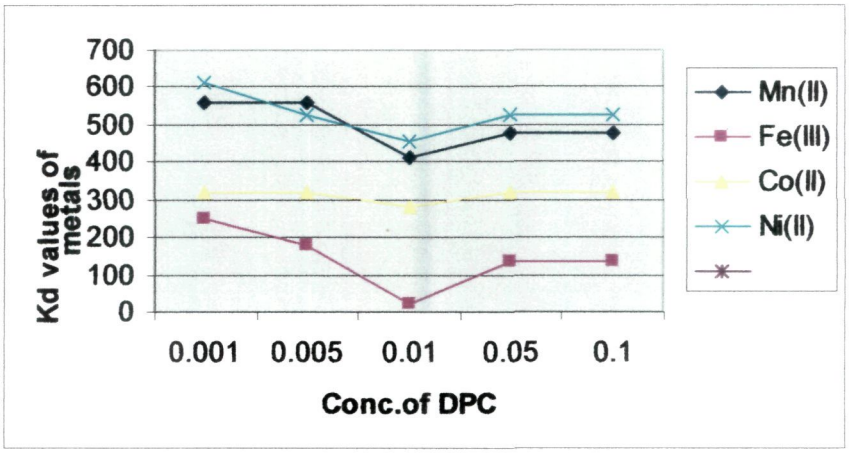


Fig. 3.6 Kd-values vs. CTAB concentrations plots for alkaline earths & heavy metals on nBACP.





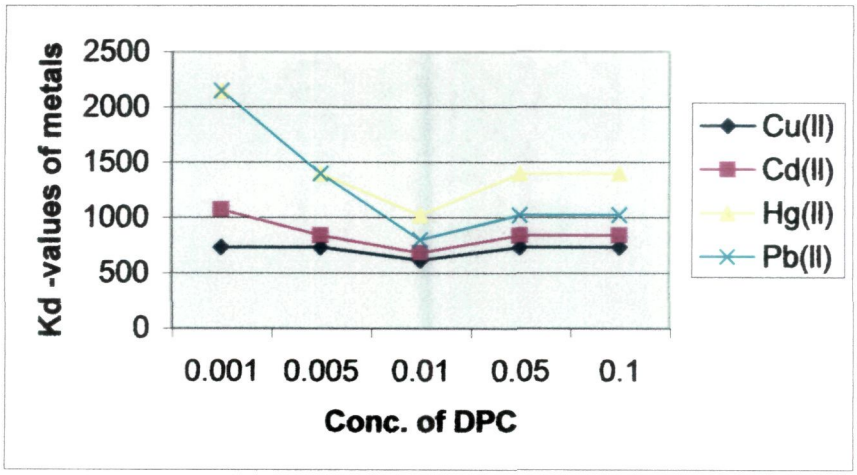
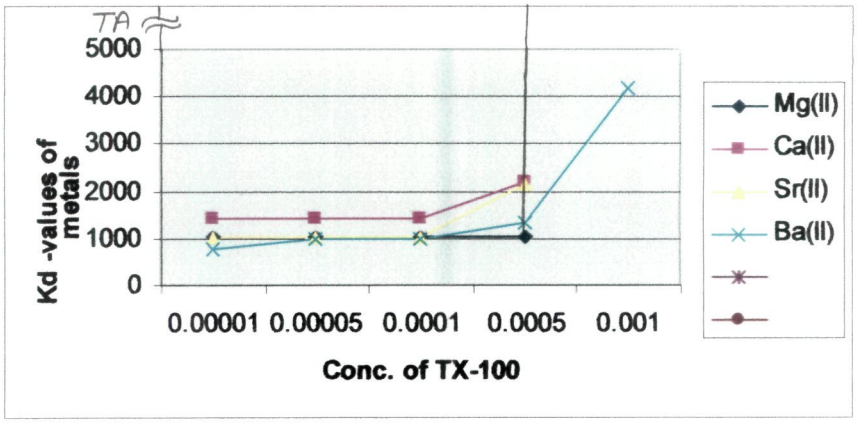
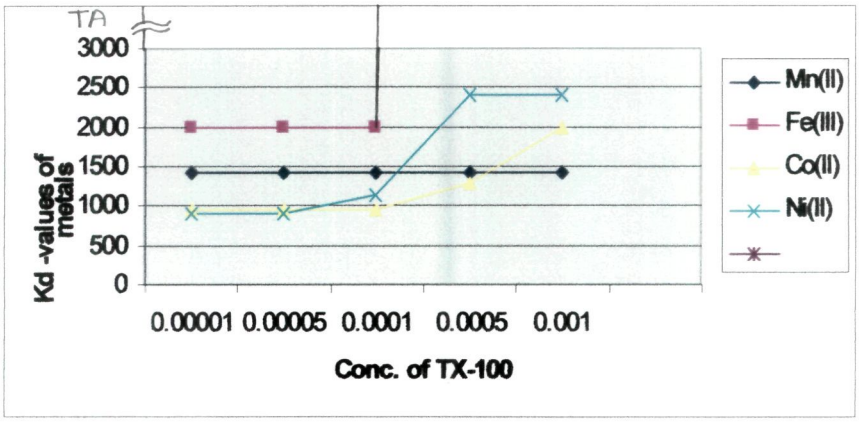


Fig. 3.7 Kd-values vs. DPC concentrations plots for alkaline earths & heavy metals on nBACP.





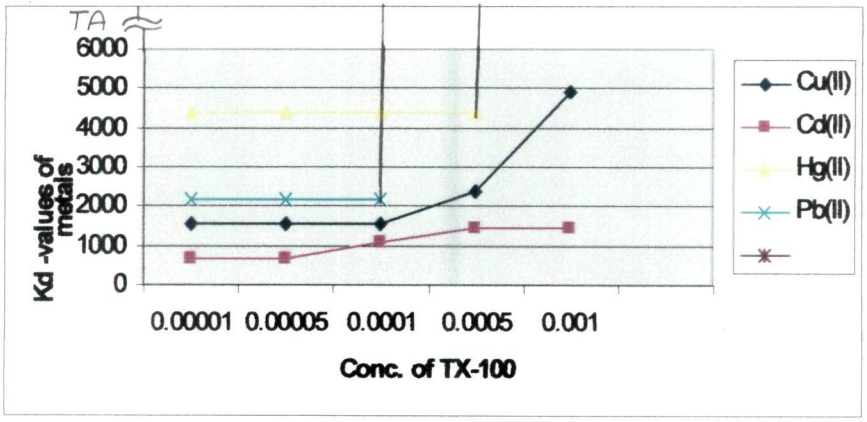
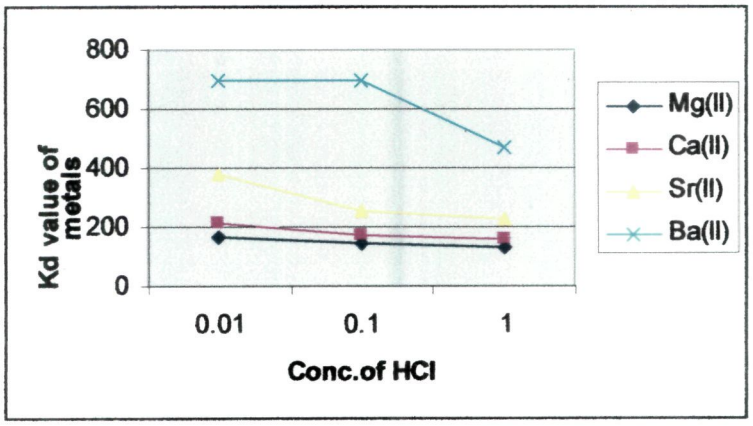
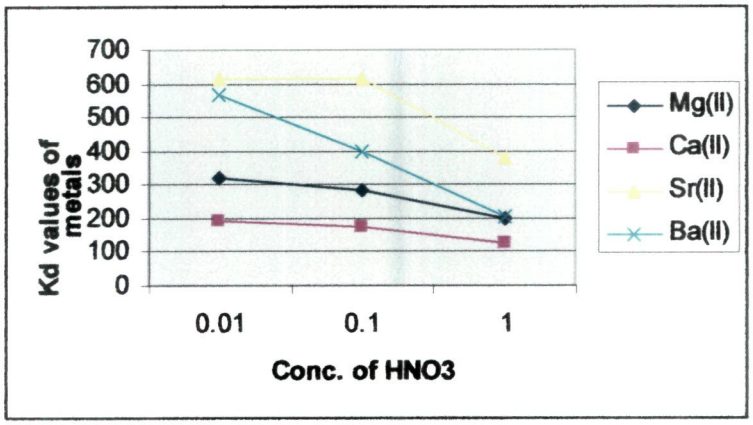


Fig. 3.8 Kd-values vs. TX-100 concentrations plots for alkaline earths & heavy metals on nBACP.





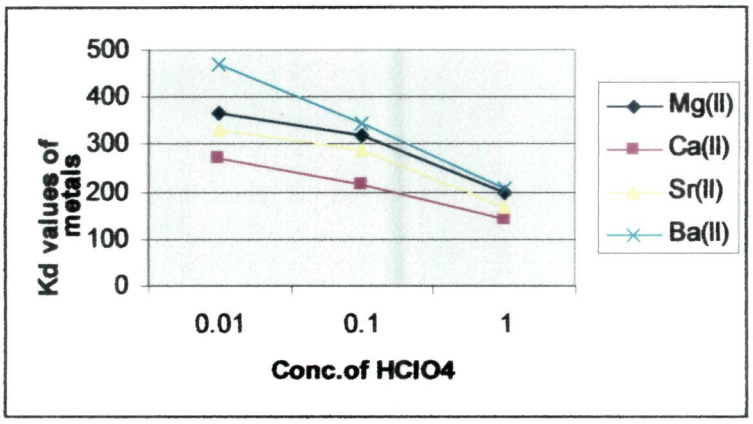
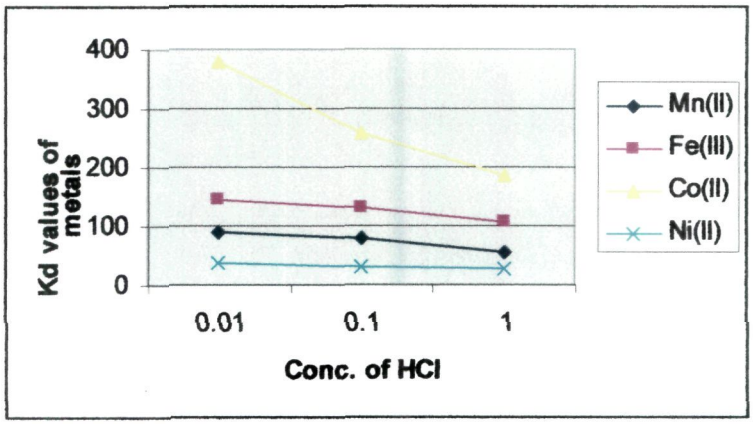
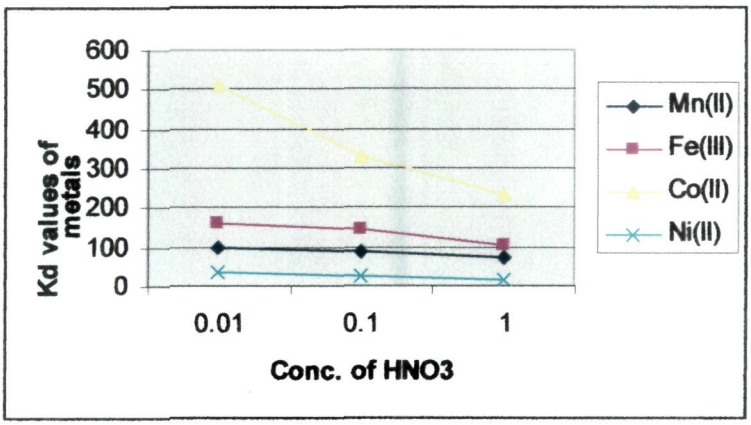


Fig. 3.9 Kd-values vs. acid concentrations plots for alkaline earths on SnP.





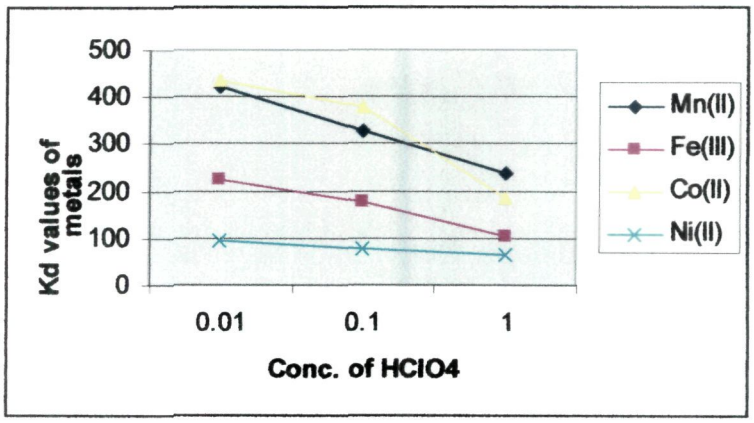
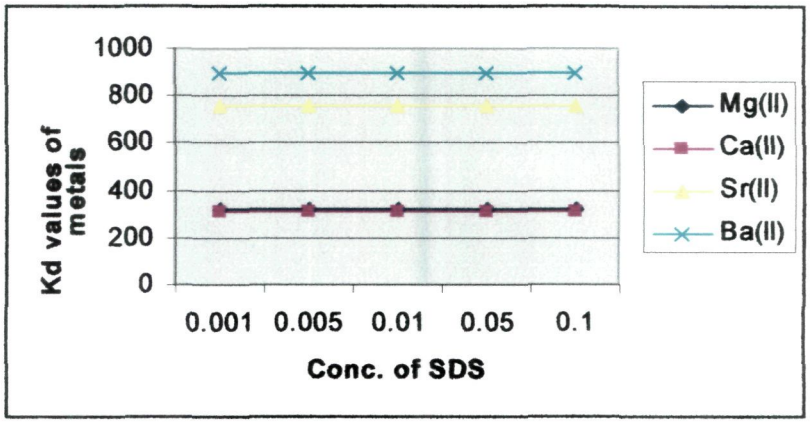
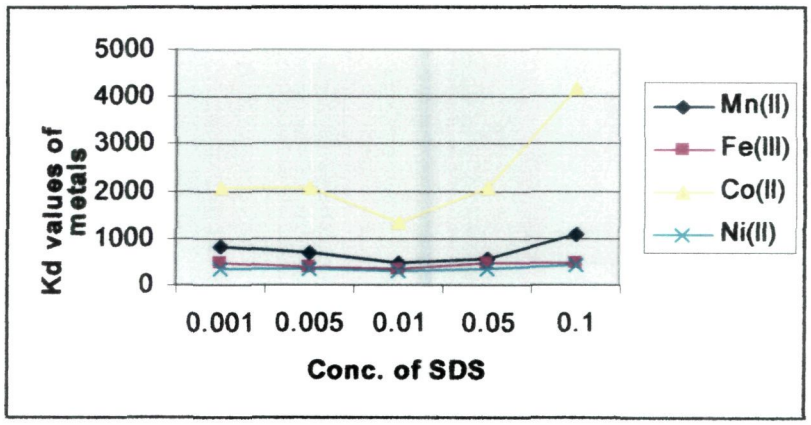


Fig. 3.10 Kd-values vs. acid concentrations plots for heavy metals on SnP.





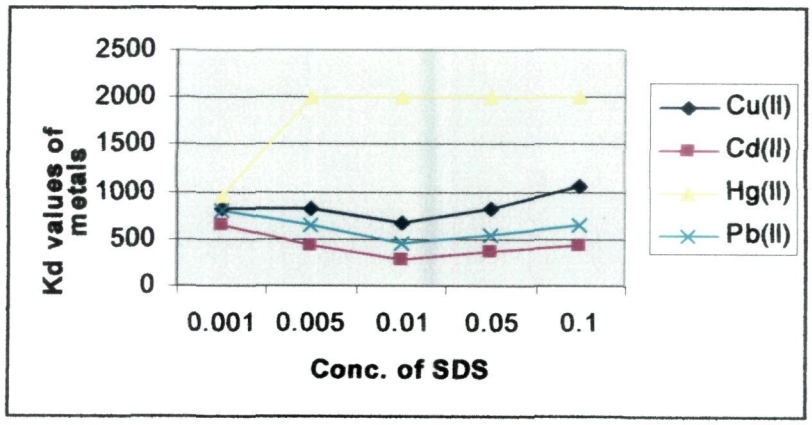
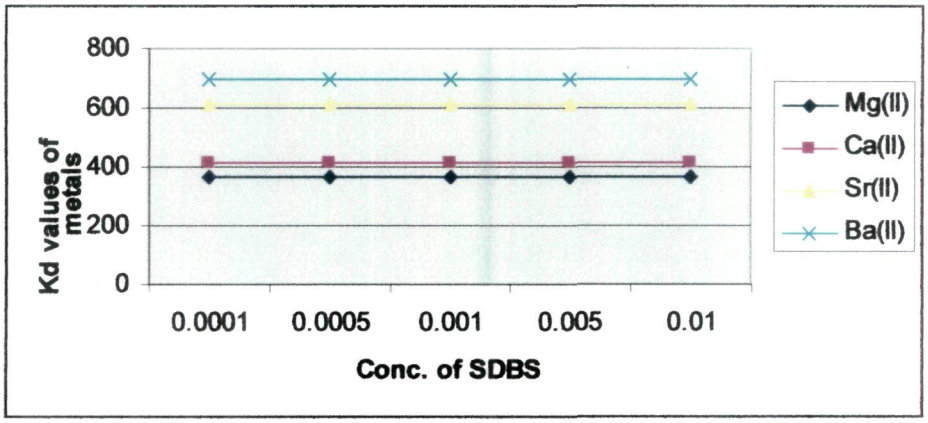
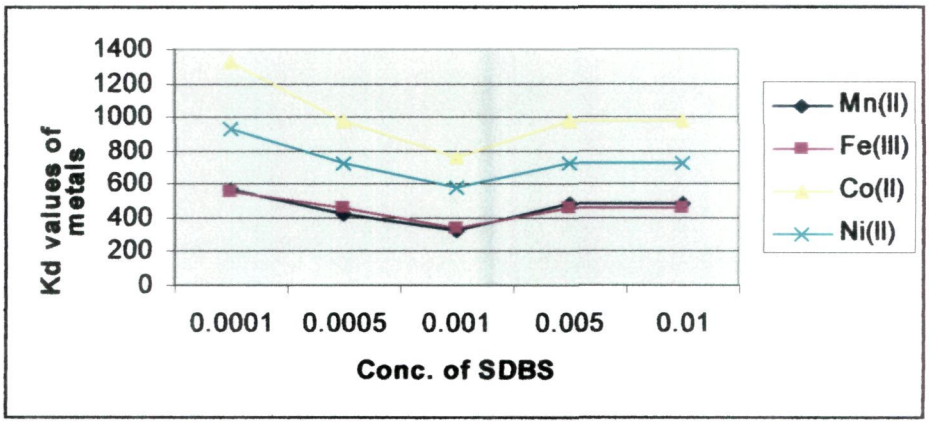


Fig. 3.12 Kd-values vs. SDS concentrations plots for alkaline earths & heavy metals on SnP.





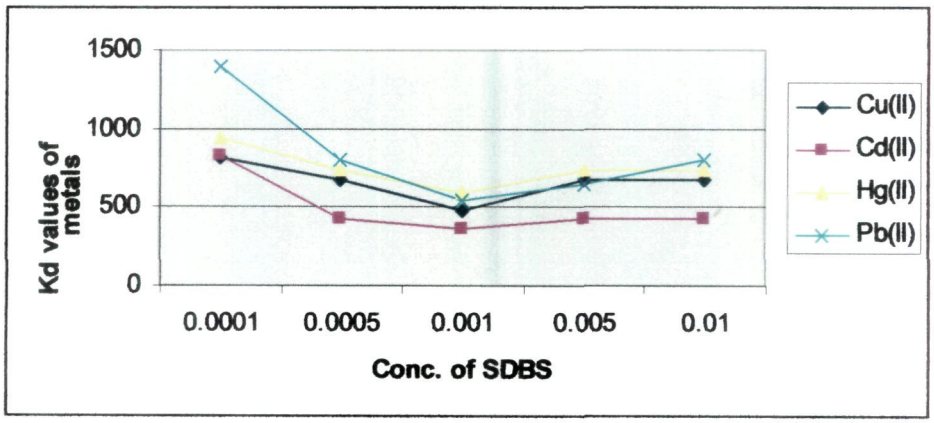
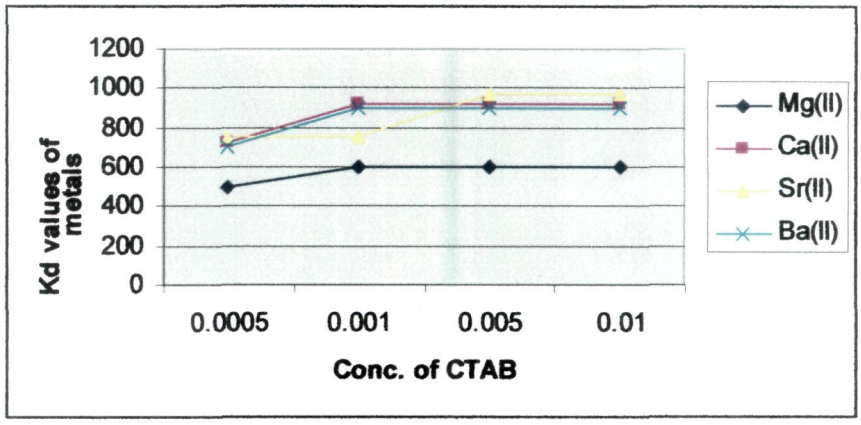
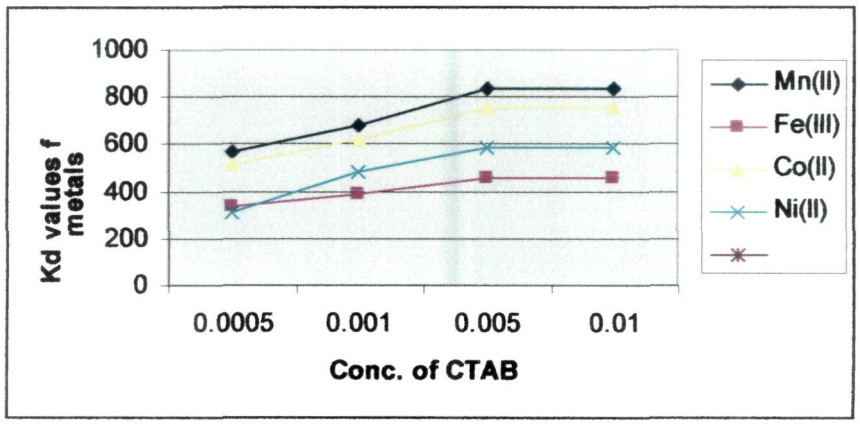


Fig. 3.13 Kd-values vs. SDBS concentrations plots for alkaline earths & heavy metals on SnP.





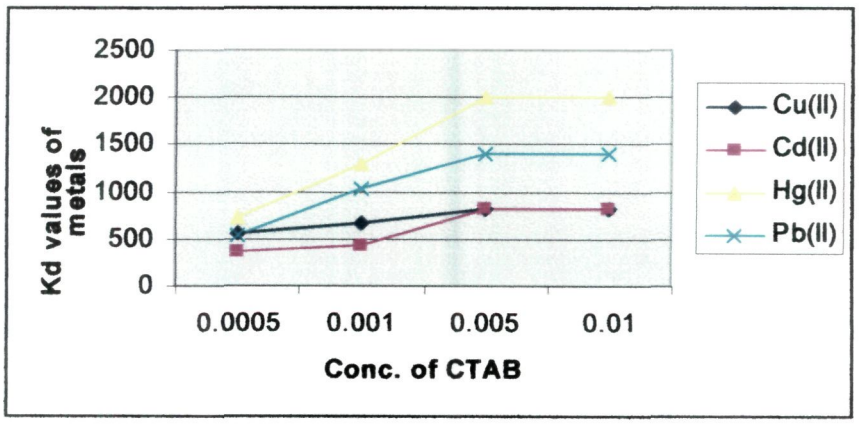
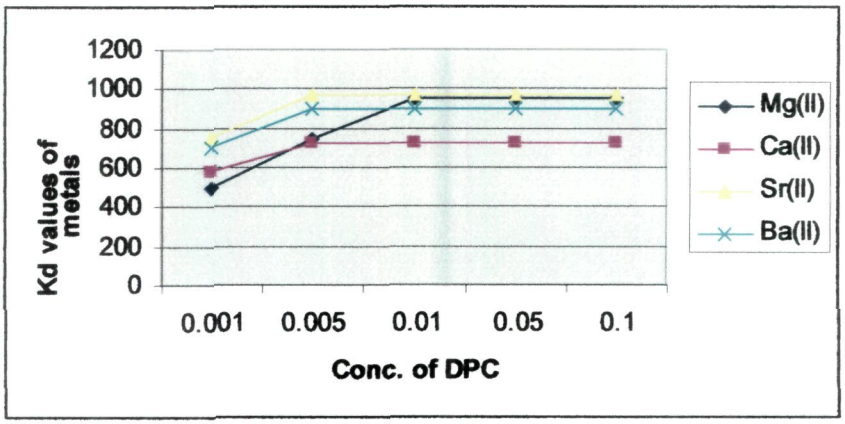
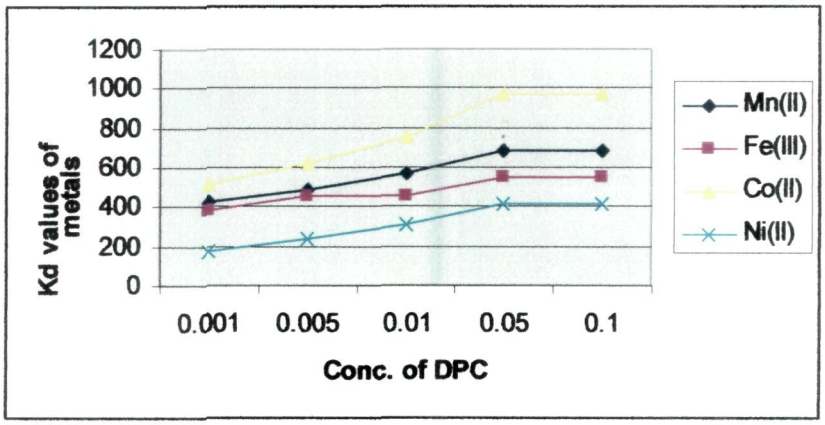


Fig. 3.14 Kd-values vs. CTAB concentrations plots for alkaline earths & heavy metals on SnP.





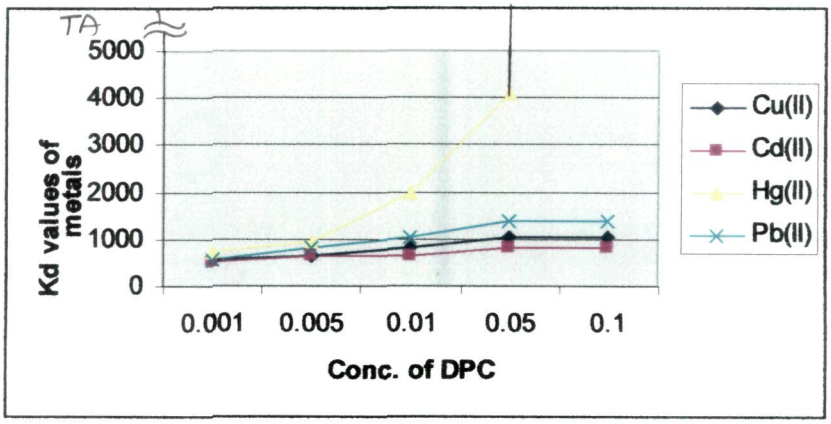
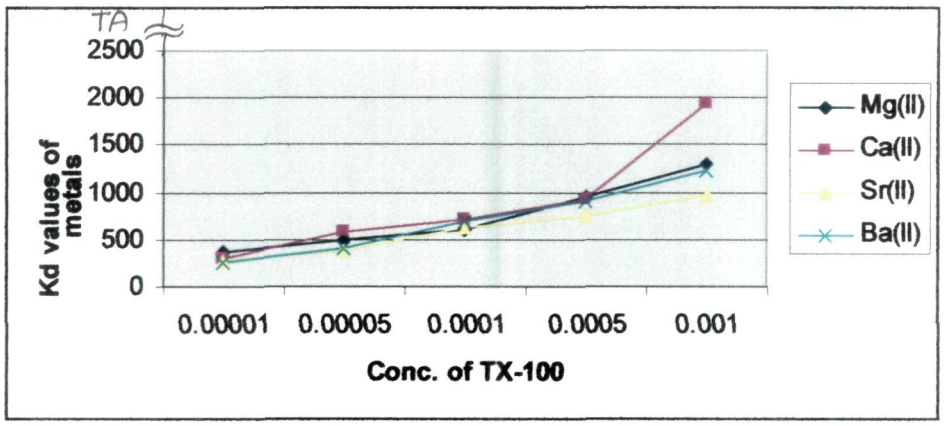
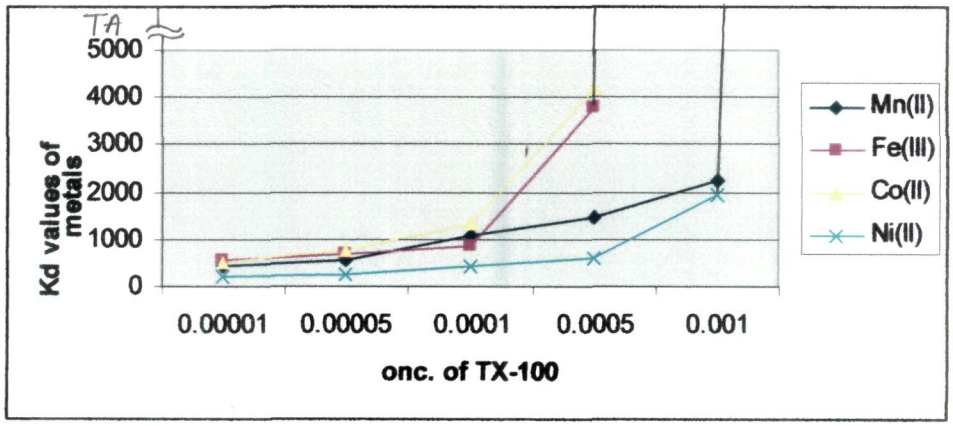


Fig. 3.15 Kd-values vs. DPC concentrations plots for alkaline earths & heavy metals on SnP.





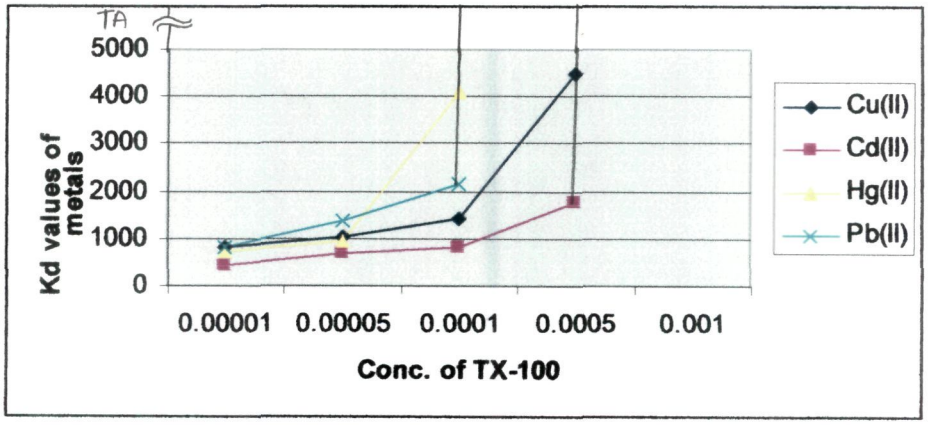


Fig. 3.16 Kd-values vs. TX-100 concentrations plots for alkaline earths & heavy metals on SnP.

3. RESULTS AND DISCUSSION

Some very interesting observations are made on the basis of the results obtained in these studies. The most salient features are as follows for the nBACP and SnP exchangers respectively:

(1) For nBACP

i) The Kd-values of different metal ions in different acid media (HCl, HNO_3 & $HClO_4$) (given in Fig. 3.1 to 3.3), decrease as the concentration of the acids increases. It is a usual behaviour of any ion exchanger.

ii) In anionic surfactants (SDS, SDBS) (given in Fig. 3.4 & 3.5), the Kd-values of alkaline earths remain constant throughout the surfactant concentrations used in these studies and the Kd-values of heavy metal ions increase upto the CMC value of the surfactants and then decrease, except Hg (II) in SDS solutions and Mn (II) in SDBS solutions. The Kd-values of alkaline earths are found to be higher, in general, as compared to the ones in different acids. The Kd-values of heavy metals increase to a greater extent in these media than in different acid media. However, Fe(III), Ni(II) and Cu(II) are the exceptions. The higher adsorption of Hg(II), Pb(II), Cd(II) and Mn(II) may be due to the complex formation of these metals with the hydrophobic part of these surfactants.

iii) In case of cationic surfactants (CTAB, DPC) (given in Fig. 3.6 & 3.7), the Kd-values of the metal ions decrease upto the CMC value, then increase and become almost constant. The Kd-values of alkaline earths are appreciably high at below and above the CMC values of the surfactants. They increase to a smaller extent as compared to the different acid media. The Kd-values of heavy metal ions are also found to be of the same order. However, they increase to a greater extent as compared to the acid media.

iv) In the nonionic surfactant (TX-100) (given in Fig. 3.8), the Kd-values remain constant upto the CMC value except Ba(II), Ni(II) and Cd(II) and then increase. Total adsorption is observed for most of the metal ions above the CMC value of the TX-100. In case of Ba(II), Ni(II) and Cd(II), the Kd-values slightly increase at the CMC value. On comparing with the acid media it is found that the adsorption of the both alkaline earths and heavy metals is higher in TX-100 than in acids. Further, the Kd-values increase to a greater extent than in the acid media. Fe (III) however, shows an exception. It is poorly adsorbed in different acid media as well as in anionic and cationic surfactants. But, in TX-100 it is totally adsorbed above its CMC value.

(2) For SnP

In case of SnP also, which is a non-fibrous ion exchanger, the adsorption behaviour for all the metal ions are found to be almost similar with the following exceptions.

(i) In anionic surfactants (given in Fig. 312 & 3.13), the Kd-values of heavy metals decrease upto the CMC value and then increase except Hg(II) in SDS solution.

(ii) In cationic surfactants (given in Fig.3.14 & 3.15), the Kd-values of alkaline earths increase upto the CMC value of the surfactants and then become constant. For heavy metals, the Kd-values increase upto a concentration slightly above the CMC value and then become constant.

(iii) In the nonionic surfactant (TX-100) (given in Fig. 3.16), the overall trend has been an increase in Kd-values with the increase in the concentration of TX-100 with some exception. For example, amongst the alkaline earth Ca(II) is found to be adsorbed to an extra ordinary high extent at the TX-100 concentration of 0.001M. Similarly, the heavy metal ions, except Mn(II) and Ni(II), show a total adsorption above the CMC value. It may be due to the positively charged complexes formed between TX-100 and heavy

metal ions above the CMC values. which may be completely adsorbed on a cation exchanger.

The orders of adsorption of alkaline earths and heavy metal ions in different acid and surfactant media are summarized in Table 3.14-3.17. As it is clear from these results and the results discussed above, there is no definite order of preferential adsorption of the metal ions. There may be so many reasons for this uneven trend, the most important being the amorphous nature of the ion exchange materials, synthesized in there studies, and the complex nature of the ion exchanger matrix. The exchanger consists of the inorganic salts such as Ce(IV) phosphate and Sn (IV) phosphate and the organic polymeric part which may be behaving differently with the metal ions in different media. The different adsorption capability of the surfactants with the metal ions may be another reason of this irregular behaviour. Thus, the various factors which may be affecting the ion exchange processes taking place, in the presently studied materials may be the following:

1. Ion exchange characteristics of the inorganic part of the material.
2. Ion exchange characteristics of the surfactants which are governed by its complex forming or the metal counter ion binding ability.
3. The polymeric nature of the organic phase of the exchanger.
4. The ionic and hydrated radii of the exchanging ions.

5. pH of the media.

All these factors are to be studied in detail before a definite conclusion may be drawn regarding the effect of surfactants on the adsorption behaviour of the hybrid type of the ion exchangers.

Table 3.14 Order of adsorption of alkaline earths on nBACP and SnP in different acid concentrations

Exchanger / Acid concentration	Decreasing order of the Kd-values	
	nBACP	SnP
0.01 M HCl	Mg>Ca≥Ba≥Sr	Ba>Sr>Ca>Mg
1 M HCl	Mg>Ca>Ba>Sr	Ba>Sr>Ca≥Mg
0.01 M HNO_3	Mg>Sr≥Ba≥Cr	Sr≥Ba>Mg>Ca
1 M HNO_3	Mg>Ba>Ca>Sr	Sr>Ba≥Mg>Ca
0.01 M $HClO_4$	Mg≥Sr≥Ca≥Ba	Ba>Mg>Sr>Ca
1 M $HClO_4$	Mg≥Ba>Ca≥Sr	Ba≥Mg>Sr≥Ca

Table 3.15 Order of adsorption of heavy metals on nBACP and SnP in different acid concentrations

Exchanger / Acid concentration	Decreasing order of the Kd-values	
	nBACP	SnP
0.01 M HCl	Ni>Hg>Co>Cu>Cd≥Mn>Fe≥Pb	Cu≥Hg>Co>Cd>Pb≥Fe>Mn>Ni
1 M HCl	Hg>Cu≥Cd>Co>Pb>Ni≥Mn>Fe	Hg≥Cu>Co≥Cd>Pb≥Fe>Mn>Ni
0.01 M HNO_3	Cd≥Hg>Cu>Mn≥Fe>Pb>Co>Ni	Co≥Hg>Pb≥Cu>Cd≥Fe>Mn>Ni
1 M HNO_3	Cd≥Hg>Cu>Fe>Co>Mn≥Ni>Pb	Hg≥Cu≥Pb>Co>Cd≥Fe>Mn>Ni
0.01 M $HClO_4$	Hg>Fe>Cd≥Cu>Pb>Mn>Co≥Ni	Hg>Pb>Cu>Co≥Mn>Fe>Cd>Ni
1 M $HClO_4$	Hg>Cu≥Fe>Cd>Mn≥Ni>Pb≥Co	Hg>Pb>Cu≥Mn>Co≥Cd≥Fe>Ni

Table 3.16: Order of adsorption of alkaline earths on nBACP and SnP in different surfactants concentrations

Exchanger / Acid concentration	Decreasing order of the Kd-values	
	nBACP	SnP
0.001 M SDS	Ba>Sr>Mg = Ca	Ba>Sr>Mg≥Ca
0.1 M SDS	Ba>Sr>Mg = Ca	Ba>Sr>Mg≥Ca
0.0001 SDBS	Ca≥Sr≥Ba>Mg	Ba>Sr>Ca>Mg
0.01 M SDBS	Ca≥Sr≥Ba>Mg	Ba>Sr>Ca>Mg
0.0005 M CTAB	Ca>Mg≥Ba>Sr	Sr≥Ca≥Ba>Mg
0.01 M CTAB	Mg = Ca≥Ba>Sr	Sr≥Ca≥Ba>Mg
0.001 M DPC	Ca≥Sr>Mg>Ba	Sr≥Ba>Ca≥Mg
0.1 M DPC	Sr>Ca>Mg>Ba	Sr≥Mg≥Ba>Ca
0.00001 M TX-100	Ca>Mg≥Sr>Ba	Mg≥Ca≥Sr≥Ba
0.001 M TX-100	Mg = Ca = Sr > Ba	Ca>Mg≥Ba>Sr

Table 3.17: Order of adsorption of heavy metals on nBACP and SnP in different surfactants concentrations

Exchanger / Acid concentration	Decreasing order of the Kd-values	
	nBACP	SnP
0.001 M SDS	Hg=Pb>Mn>Cd>Co>Cu>Ni≥Fe	Co>Hg>Mn≥Cu≥Pb>Cd>Fe>Ni
0.1 M SDS	Pb>Cd>Co>Hg>Mn>Cu>Ni>Fe	Co>Hg>Mn≥Cu>Pb>Fe≥Cd≥Ni
0.0001 SDBS	Hg>Mn≥Cd>Pb>Co≥Cu>Fe>Ni	Pb≥Co>Hg>Ni>Cd>Cu>Mn≥Fe
0.01 M SDBS	Cd≥Pb>Co>Cu>Hg≥Ni>Fe>Mn	Co>Pb>Hg≥Ni>Cu>Mn≥Fe≥Cd
0.0005 M CTAB	Pb>Hg≥Cu≥Cd>Mn>Ni>Co>Fe	Hg>Mn≥Cu≥Pb≥Co>Cd≥Fe≥Ni
0.01 M CTAB	Pb≥Cu≥Hg>Cd≥Mn>Ni≥Co>Fe	Hg>Pb>Mn≥Cd≥Cu>Co>Ni>Fe
0.001 M DPC	Hg=Pb>Cd>Cu>Ni>Mn>Co>Fe	Hg>Cu≥Pb≥Cd≥Co>Mn>Fe>Ni
0.1 M DPC	Hg>Pb>Cd>Cu>Ni>Mn>Co>Fe	Hg>Pb>Cu>Co>Cd>Mn>Fe>Ni
0.00001 M TX-100	Hg>Pb>Fe>Cu≥Mn>Co≥Ni>Cd	Cu≥Pb>Hg>Fe≥Co>Cd≥Mn>Ni
0.001 M TX-100	Fe=Hg=Pb>Cu>Ni≥Co>Cd≥Mn	Fe=Co=Cu=Cd=Hg=Pb>Mn>Ni

The adsorption mechanism of the metal ions on an ion exchange material in presence of surfactants can be explained on the basis of micellar association in terms of the electrostatic model, i.e., Gouy-Chapman electrical double layer approaximation[7-10], or in terms of the counter ion binding approximation.[11] In electrostatic model, two reactions depicting the metal complex formation have been studied; one taking place entirely at the micellar surface and the other in the bulk phase between the micelles. The micellar/solvent interface consists of Stern layer containing the ionic surfactant heads and a certain amount of adsorbed counter ions which lower the apparent charge density of the micelle and of a diffused layer. Therefore, the spatial distribution of the counter ions in the neighbourhood of charged micelles is influenced by the charge density of the polyions[12], size of the ions, their hydration and the variation of dielectric constant. Further, the binding of hydrophilic ions is controlled by electrostatic interactions.[13] Ions having a charge, opposite, to the surfactant head groups (counter ions) are attracted to the micelle surface while reverse is true for the co-ions. Binding of amphiphilic ions is governed by hydrophobic and electrostatic effects; additive for counter ions, but opposed for co-ions.

The increase of the Kd-values of heavy metal ions upto the CMC value and then decrease on nBACP, in presence of anonic surfactants (SDS & SDBS) may be due to the increasing charge density of the surfactant monomers upto the CMC value. After CMC, the micelles start forming lowering the apparent

charge density thus resulting the decreased Kd-values (Except Hg). The density of adsorbed counter ions remains smaller than the density of polar heads and each adsorbed ion stands close to a polar head; in order to cancel its charge. But, in all the considered metals, Hg(II) has the highest density (as given is Table 3.18). Therefore, it gives a exceptional order of Kd-values. The constant Kd-values of alkaline earths can be explained by an ion exchange model which assumes that the micelles surface binds counter ions selectively[14,15] or, these alkaline earths have the ionic radius about equal to the Na^+ ions (given in Table 3.18) so, are not associated in micelles.

The Kd-values of metal ions with nBACP in presence of catinic surfactants (CTAB, DPC) decrease upto the CMC value then increase. This may be due to the fact that the metals are not associated with surfactant monomers due to the presence of co-ions but beyond the CMC value, in micelles some oppositively charged counterions attract the metal ions present in diffused as well as in Stern layer, as a result of which Kd-values increase.

Additionally, for nonionic surfactants[16], metal ions can occur in the polyoxyethylene shell of the surfactant. As a result the adsorption of metal ions on SnP and nBACP increase and reach to the maximum. Here most of metal ions get total adsorption.

Micelles are not rigid but highly mobile in spite of their aggregated structure. They exist in a dynamic equilibrium with the free monomers.[17] The lifetime of a monomer in the micelle is about 10^{-5} sec.[18]. The intramolecular

motions of monomers within the micelle can be assumed to be rather unrestricted with an enhanced mobility of the terminal alkyl group predominantly oriented with in the micellar core and of the ionic head groups situated at the surface of the micelle.[19] Correlation limits of these motions are considerably shorter than residence times of individual monomers in the micelle. Thus, for a process, where a characteristic time range slower than that of the ionic head group mobility, the micelles appear to be a sphere uniform smeared-out surface charge. As a result, a constant surface potential can be assigned to the micellar surface. Such condition arises in the case of adsorption of heavy metals on Sn(IV) phosphate in presence of surfactants. With anionic surfactants, the Kd-values of metal ions decrease till CMC then increase while the Kd-values should increase till CMC then decrease according to charge density of the polyions. And in presence of cationic surfactants, the adsorption of metal ions on Sn(IV) phosphate increases and above CMC becomes constant.

Finally, from the results, given before, we may conclude that the surfactants increase the adsorption of metal ions to a greater extent on Sn (IV) phosphate, a non fibrous material as compared to the n-butyl acetate Ce(IV) phosphate, a fibrous material.

Table. 3.18 The Ionic radius and density of metal ions.[20]

Metal ions	Ionic radius (Å)	Density (g cm^{-3})
Na^{+}	1.02	0.97
Mg^{++}	0.72	1.74
Ca^{++}	1.0	1.55
Sr^{++}	1.18	2.63
Ba^{++}	1.35	3.62
Mn^{++}	0.67	7.43
Fe^{+++}	0.64	7.87
Co^{++}	0.74	8.9
Ni^{++}	0.69	8.91
Cu^{++}	0.73	8.95
Cd^{++}	0.95	8.65
Hg^{++}	1.02	13.534
Pb^{++}	1.20	11.40

References

1. G. Alberti and U. Costantino, J. Chromatogr., 102, 5, (1974).

2. G. Alberti, M.A. Massucci and E. Torracca, J. Chromatogr., 30, 579 (1967).

3. G. Alberti, M. Casciola, U. Costantino and M.L. Luciani Giovagnotti, J. Chromatogr., 128, 289, (1976).

4. J.J. Trivedi, B.T. Mandalia and D.R. Baxi, Proc. Ion-exchange Symposium, Bhavnagar, India, Gadre, G.T., Ed., Sahitya Mudranalaya. Ahmedabad, 22, 5 (1979).

5. U. Costantino and A. Gasperoni, J. Chromatogr., 51, 289 (1970).

6. M.J. Fuller, J. Inorg. Nucl. Chem., 33, 559 (1971).

7. N.A. Mazer, M.C. Carey, G.B. Benedek, J. Phys. Chem., 80, 1075 (1976); in "Micellization, Solubilization and Microemulsions", K.L. Mittal, Editor, vol.1, p.359, Plenum Press, New York, 1977.

8. P.J. Missel, N.A. Mazer, G.B. Benedek, C.Y. Young and M.C. Carey. J.Phys. chem.., 84, 1044 (1980).

9. P. Murkerjee and A. Ray, J. Phys. Chem. 70, 2149 (1966).

10. P.J. Missel, N.A. Mazer, M.C. Carey and G.B. Benedek in "Solution behaviour of surfactants – Theortical and Applied Aspects", K.L. Mittal and E.J. Fendler, Editors, Vol.1, pp.373-388, Plenum Press, New York (1982).

11. G. Porte and J. Appell, J. Phys. Chem., 85, 2511 (1981).

12. M. Fixman, J. Chem. Phys., 70, 4995 (1979).

13. B. Lindman and H. Wennerstrom, Topics Curr. Chem., 87, 1 (1980).

14. L.S. Romsted, Ph.D. Thesis, Indiana Univ. (1975).

15. L.S. Romsted in "Micellization, Solubilization and Microemulsions", K.L. Mittal Editor, Vol.2, p.509, Plenum Press, New York, 1977.

16. J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular systems, Academic Press, New York, (1975).

17. M.R. Porter, Handbook of Surfactants, IInd Ed., U.K., 1994.

18. S. Diekmann, Ber. Bunsenges, Phys. Chem.. 83, 528 (1982).

19. E. Lessner and J. Frahm, J. Phys. Chem. 86, 3032 (1982).

20. J.D. Lee, Concise Inorganic Chemistry, 5th Ed., Chapman & Hall Ltd., London (1996).